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STATE OF THE ART
REVIEW ON PRODUCT RECOVERY

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STATE OF THE ART REVIEW ON PRODUCT RECOVERY

by

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for the

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
DEPARTMENT OF THE INTERIOR

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TABLE OF CONTENTS

	Page
Table of Contents	iii
Abstract	iv
List of Figures	v
List of Tables	vi
Summary	vii
Introduction	1
Economic, Technical and Philosophical Framework	3
Pulp and Paper Mills	5
Steel Industry	17
Plating and Allied Industries	25
Mining Industry	29
Coal By-Products	33
Coke and Gas Industry	33
Flue Gas Treatment	33
Petroleum Industries	37
Petrochemical Industries	37
Petroleum Refineries	38
Recovery of Oil From Waste Waters	40
Sludge Disposal and By-Product Recovery	46
Heat Recovery or Utilization	49
Miscellaneous Industries	50
Breweries and Distilleries	50
Food Industries	50
Fertilizer Industry	53
Animal Products	56
Organic Chemicals Industry	61
Textile Industry	71
Nuclear Plants	72
Milk Industry	73
Inorganic Chemicals Industry	73
Appendix I - General Methods of Treatment and Recovery	78
Appendix II - Other Chemical Reactions of Interest	81
Appendix III - Physical Methods of Treating Gaseous Wastes	86
References	88

ABSTRACT

This report on "State of the Art Review on Product Recovery" covers the recovery, reuse and/or sale of materials recovered from liquid effluents or produced as a result of the treatment of liquid effluents. A critical and complete review of literature up to date on product recovery in major water use industries is presented. The economical, technical and philosophical framework which determines the application of product recovery is presented wherever possible. This report does not cover water renovation for reuse and product recovery from solid wastes. However, an evaluation of the utilization and product recovery of municipal sludge is presented. The principal areas of discussion are: waste reduction practices including in-plant control, recovery techniques and practices, practical operating problems and the relationship between recovery and treatment.

The report concludes that:

1. Product recovery is an accepted practice with increasing usage.

2. Industry needs increasingly complex processes to develop optimum recovery schemes.

3. By-product recovery generally results in a net cost to industry generally of a smaller magnitude than conventional treatment.

4. The situation is complicated by the tax exemption laws.

LIST OF FIGURES

Page

1. USEFUL RANGES OF VARIOUS SEPARATION PROCESSES viii

2. - 6. UNIT PROCESSES AND BY-PRODUCTS RECOVERED IN THE MAJOR WATER USE INDUSTRIES ix-xiii

7. PRESENT STATUS OF RECOVERY CYCLE 6

8. PULP AND FIBER RECOVERY IN A BOARD MILL 10

9. HOLOPULPING PROCESS 13

10. RECOVERY OF SULFURIC ACID AND IRON FROM WASTE PICKLE LIQUOR IN THE STEEL INDUSTRY 18

11. EVAPORATION - CRYSTALLIZATION (S.A. LAURICK - STRUTHERS - WELLS CORP.) 19

12. PICKLING REGENERATION CYCLE 22

13. FLOW DIAGRAM OF BIOCHEMICAL OXIDATION AND LIMESTONE NEUTRALIZATION PROCESS 31

14. PROCESS FLOW SHEET OF FLUE GAS TREATMENT 35

15. RECOVERY OF SOLUBLE OIL FROM RECLAIMED OIL 45

16. BASIC PROCESSES IN THE MEAT-PACKING INDUSTRY 57

17. FLOW DIAGRAM OF KEL-CHLOR PROCESS 67

18. INCINERATION - SCRUBBING SYSTEM (UNION CARBIDE) 69

LIST OF TABLES

Page

I. BY-PRODUCT RECOVERY IN THE PULP AND PAPER MILL INDUSTRIES 16

II. BY-PRODUCT RECOVERY IN THE IRON AND STEEL INDUSTRIES 24

III. BY-PRODUCT RECOVERY IN PLATING AND ALLIED INDUSTRIES 28

IV. BY-PRODUCT RECOVERY IN COAL BY-PRODUCTS INDUSTRY 36

V. BY-PRODUCT RECOVERY IN THE ORGANIC CHEMICALS INDUSTRY 70

VI. BY-PRODUCT RECOVERY IN THE INORGANIC CHEMICALS INDUSTRY 77

A-I. CHEMICAL OXIDANTS AND AREA OF USE 80

SUMMARY

Product recovery from waste waters is an accepted practice from an economical and pollution control point of view. In many cases, recovery of by-products is not practiced as it is cheaper to dump the wastes rather than to process them. But with the increasing environmental control legislation and enforcement, product recovery technique is gaining high importance.

The urgent problem facing the industries is how to recover by-products from waste materials and what to do with them. Sophisticated methods have been developed for the separation of products of different sites and a chart showing the ranges of various separation processes is presented in Figure 1. The various unit processes used in the recovery of by-products and the products recovered are shown in Figures 2-6. These unit operations are typical and can be applied in the various industries wherever applicable.

The practice of product recovery results in a net cost to the industry, but it has been proven frequently to be cheaper than other methods of disposal. The choice of a method of treatment depends on the economic considerations and degree of treatment desired. Removal of pollutants to the desired level is generally achieved through conventional processes, but it should be realized that the same degree of treatment can be achieved either by product recovery alone or by a combination of product recovery and conventional treatment processes. Advantage of reducing pollutional load through product recovery consists in the overall reduction of the cost of treatment and conservation of natural resources.

Unfortunately, the entire thrust of taxation and regulation has been negative with regard to by-product recovery. Too many of the state regulations are promulgated and permits issued with a specific reduction in a pollutant level regardless of the amount of discharge. Therefore, a company may eliminate a substantial quantity of pollutant by by-product recovery and still find itself faced with the same degree of required removal although on a smaller quantity. This has the effect of eliminating part of the benefit of by-product recovery. Only when recovery reaches 100% (a very unusual case) can total recovery of waste costs be achieved.

This problem is complicated by the fact that all pollution control facility tax exemption laws enacted in this country specifically exclude credits for facilities which recover any product for reuse or sale.

Thus, while it can be argued that while the social good of the

FIGURE I

USEFUL RANGES OF VARIOUS SEPARATION PROCESSES

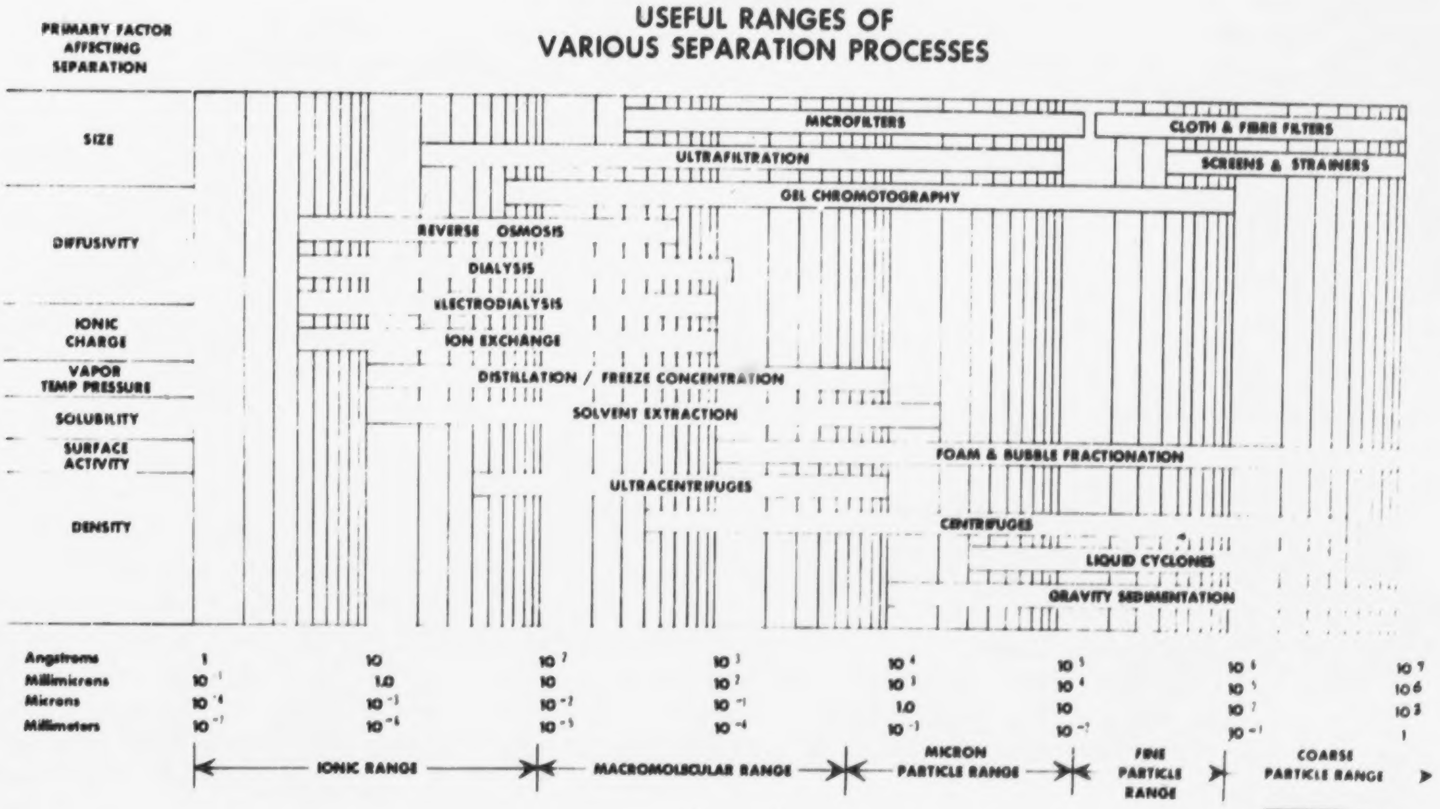

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FIGURE 2

UNIT OPERATIONS AND PRODUCTS RECOVERED IN MAJOR WATER USE INDUSTRIES

INDUSTRY	LIQUID - LIQUID			
	DISTILLATION	ADSORPTION	ABSORPTION	CRYSTALLIZATION
PAPER AND PULP MILLS	Recovery of pine oil from sulfate turpentine;Recovery of Methanol from evaporated black liquor solids	Recovery of S from SO_2	Recovery of S from SO_2	Recovery of sulfate turpentine;Recovery of Na_2CO_3 and $NaHCO_3$
STEEL INDUSTRY		Removal of fluorides	Recovery of NH_3, Recovery of HCl	
PLATING INDUSTRY				
MINING INDUSTRY	Production of pigment producing organometallic compounds	Recovery of molybdic oxide		
COKE & GAS INDUSTRIES	Recovery of Argon from Hydrogen	Recovery of H_2SO_4; Recovery of Phenol	Recovery of HCl; Recovery of nitrogen oxides	Recovery of Na_2SO_4
PETROCHEMICAL INDUSTRIES	Recovers chlorinated hydrocarbons, olefins and solvents	Separation of H_2 from Hydrocarbons; Recovery of CS_2 and CCl_4		Separation of Xylene from ethyl benzene
PETROLEUM REFINERIES	Recovery of NH_3 and H_2SO_4 from sour water for production of $(NH_4)2SO_4$			
BREWERIES & DISTILLERIES	Recovery of process water	Removal of fines		
FERTILIZER INDUSTRIES	Recovery of ammonia	Recovery of fluorides		Recovery of gypsum
ANIMAL PRODUCTS				
TEXTILE INDUSTRY				
ORGANIC CHEMICALS INDUSTRY	Recovery of phenol			Recovery of inorganics
NUCLEAR PLANTS	Recovery of plutonium and uranium			

FIGURE 3

UNIT OPERATIONS AND PRODUCTS RECOVERED IN MAJOR WATER USE INDUSTRIES

INDUSTRY	LIQUID - LIQUID			
	EVAPORATION	PRECIPITATION	SOLVENT EXTRACTION	DIALYSIS
PAPER AND PULP MILLS	Concentration of lignin for phenol recovery		Recovery of acetic and formic acids from NSSC cooking effluents	
STEEL INDUSTRY	Concentration of H_3PO_4 acid	Production of gypsum; Recovery of iron	Recovery of Phenol	Recovery of acids H_2SO_4, H_3PO_4
PLATING INDUSTRY				Recovery of Ni, Cu
MINING INDUSTRY		Recovery of copper from mine tailings; Removal of contaminating metals		
COKE & GAS INDUSTRIES			Recovery of phenol with benzene	Recovery of H_2SO_4
PETROCHEMICAL INDUSTRIES			Recovery of isobutylene, naphthalenes, parafins and phenols	
PETROLEUM REFINERIES	Concentration of H_2SO_4		Recovery of Phenol	
BREWERIES & DISTILLERIES	Drying of yeast for cattle feed		Recovery of process water	Removal of fines to improve the product
FERTILIZER INDUSTRIES	Recovery of gypsum	Recovery of NH_3 as $(NH_4)_2SO_4$; Production of synthetic cryolite or aluminum fluoride		
ANIMAL PRODUCTS				
TEXTILE INDUSTRY	Recovery of NaOH			
ORGANIC CHEMICALS INDUSTRY		Recovery of Na Salts	Recovery of phenol; Recovery of oil	
NUCLEAR PLANTS			Recovery of plutonium from metal scraps	

FIGURE 4

UNIT OPERATIONS AND PRODUCTS

RECOVERED IN MAJOR WATER USE INDUSTRIES

INDUSTRY	LIQUID - LIQUID		
	ELECTRO DIALYSIS	ION EXCHANGE	ULTRA-FILTRATION
PAPER AND PULP MILLS	Recovery of lignosulfonic acids, wood sugers and acids		Concentrating solutes, production of demineralized water
STEEL INDUSTRY	Recovery of acid and iron	Process water recovery	
PLATING INDUSTRY		Recovery of valuable metals like Au,Ag; Recovery of cyanides,chromic acids and demineralized water	Recovery of demineralized water
MINING INDUSTRY		Recovery of copper uranium from leaching solutions from copper ore waste dump; Recovery of water	Recovery of pigment producing organometallic compounds
COKE & GAS INDUSTRIES	Recovery of H_2SO_4; Recovery of Chlorine from HCl	Recovery of H_2SO_4; Recovery of Phenol	
PETROCHEMICAL INDUSTRIES		Recovery of amino acids, organic acids and alkaloids	Recovery of H_2 from petroleum effluents
PETROLEUM REFINERIES			
BREWERIES & DISTILLERIES	Removal of fines to improve the product	Refining the products	Refining the products
FERTILIZER INDUSTRIES			
ANIMAL PRODUCTS			
TEXTILE INDUSTRY			
ORGANIC CHEMICALS INDUSTRY			
NUCLEAR PLANTS		Separation of radionuclides	Separation of radionuclides

FIGURE 5

INDUSTRY	SOLID-LIQUID		
	SETTLING	THICKENING	FILTRATION
PAPER AND PULP MILLS	Concentrating pulp	Concentrating Pulp	Dewatering Sludge
STEEL INDUSTRY	Separation of oil		
PLATING INDUSTRY			
MINING INDUSTRY			
COKE & GAS INDUSTRIES			Recovery of Silica from ferro silicon plants
PETROCHEMICAL INDUSTRIES			
PETROLEUM REFINERIES			
BREWERIES & DISTILLERIES	Separation of spent hops	Separation of spent hops	
FERTILIZER INDUSTRIES			Recovery of powdered silica
ANIMAL PRODUCTS			
TEXTILE INDUSTRY			Recovery of NaOH; Recovery of process water
ORGANIC CHEMICALS INDUSTRY			
NUCLEAR PLANTS			

FIGURE 6

INDUSTRY	SOLID–LIQUID			
	CENTRIFUGATION	FLOTATION	EVAPORATION	WET SCRUBBING
PAPER AND PULP MILLS	Separation of tall oil from black liquor; Dewatering of paper mill sludge		Recovery of Na_2CO_3 and Na_2S; Production of Masonex cattle feed	Recovery of S or H_2SO_4 from SO_2
STEEL INDUSTRY	Separation of oil	Recovery of Phenol, Phosphates and heavy metals; Recovery of oil	Concentration of acids; concentration of calcium chloride	
PLATING INDUSTRY			Concentrating the waste; Concentration of H_3PO_4 acid	
MINING INDUSTRY		Recovery of fine coals	Recovery of $(NH_4)_2SO_4$	
COKE & GAS INDUSTRIES	Removal of phenol from ammonia liquor	Separation of oil from tar sands	Concentrating the acid H_2SO_4	Production of S, H_2SO_4 or SO_2 and $(NH_4)_2SO_4$
PETROCHEMICAL INDUSTRIES				Removal of CO_2 and H_2 Streams
PETROLEUM REFINERIES				Recovery of Solvents
BREWERIES & DISTILLERIES			Production of cattle feed and vitamin	
FERTILIZER INDUSTRIES				Recovery of NH_3 from exhaust gas
ANIMAL PRODUCTS	Recovery of fat and grease			
TEXTILE INDUSTRY			Recovery of NaOH	
ORGANIC CHEMICALS INDUSTRY				Recovery of HCl, Recovery of S,SO_2 and H_2SO_4
NUCLEAR PLANTS		Separation of radio nuclides		

country is in the direction of by-product recovery, the existing regulations and taxation are such as to discourage by-product recovery by industry in place of conventional waste treatment techniques. We strongly feel that a review of regulatory and fiscal policies should be made to encourage the use of recovery and reuse techniques by industry in the treatment of their wastes.

The Future

It is obvious from this study that:

1. By-product recovery already occupies an important place in the regular practice of American industry.

2. By-product recovery practice is dependent primarily upon economic factors rather than technological ones.

3. A variety of technology exists and is practiced to achieve by-product recovery in a variety of industries.

Further, it is anticipated that increased by-product recovery will occur in the future because of tighter pollution control regulations. It is not hard to justify the social desirability of by-product recovery both on the basis of reduced pollutional load and because of the decreased demands which would be created for our obviously limited natural resources. Thus, it is important to note those factors which will encourage industry to utilize by-product recovery on an increasing scale. After numerous discussions with industrial leaders, we feel that the steps outlined below, if taken, would encourage the use of by-product recovery as an anti-pollution approach and one of considerably more merit than ordinary pollution control techniques currently in practice:

1. Development of a consistent pollution control program with sharply defined objectives and a sharply defined time scale strictly enforced with controls set on discharge quantities rather than a universal removal percentage.

2. Use of tax incentives to include treatment units where by-product recovery is practiced. Special incentives should be given for material in short supply for the reuse and recovery of.

3. Development of additional technological tools for the removal of pollutants in small quantities from water, not only on a gross basis, but in a manner which will permit specific separations to be made.

4. Encouragement of pretreatment of industrial wastes prior to admission into joint systems through surcharging programs.

It is recognized that portions of these proposed steps are underway and that others may be administratively or politically difficult to undertake. However, they are necessary for optimal socio-economic goals. As a further note, it is important that industry recognize the significance of building a market for by-products just as it does for prime products. In many cases, great quantities of by-product chemicals and materials are readily available for use but the markets for them are simply not sufficiently developed to totally accept the available supply. If markets have not been developed, maximum by-product recovery will not be feasible or practiced.

Both industry and government must become attuned to a "waste not want not" philosophy in the future in order to preserve the environment and our natural resource base.

Most industrial leaders agree that recovery and use is highly practical in many circumstances because industrial wastes can be separated by unit (at least in newer plants) and the wastes are largely product, feed or by-product. The pressure for reuse will be strongest in the case of conservative species which, when regulations are enacted and enforced, will have to be concentrated and disposed of in some fashion. If concentration is necessary in any case, then recovery and reuse seems to be an economically viable approach in handling this type of waste in the future.

INTRODUCTION

This report on the "State of the Art Review on Product Recovery" is based on an exhaustive literature review, discussions with various outside sources including industrial organizations actively engaged in product recovery activities and the experience of the principal investigator, associates and consultants of Resource Engineering Associates.

Considerable literature[1-12] already exists with regard to water reuse and by-product recovery although no complete presentation of the current status of by-product recovery exists in the literature.

This report was developed on the basis of an extensive literature search based on Chemical and Engineering Abstracts as well as a complete review of all existing literature in the fields of chemical and sanitary engineering. The reports prepared by the USPHS and FWPCA were also reviewed and numerous contacts were made with industries with practical experience in by-product recovery.

The report summarizes, industry by industry, the current status of by-product recovery. In addition, the Appendix contains three chapters which review the process technology as related to by-product recovery.

The purpose of this report is to summarize the technical and practical extent of by-product recovery as practiced in this country.

The concept of product recovery is gaining far more widespread utilization than in the past because of the press and expense of increasingly tight environmental control legislation and regulations. Such an approach is being encouraged by both industries and governmental agencies for the following reasons:

1. A general reduction of the level of industrial pollutant discharge.

2. The possibility of reducing overall environmental control expenditures.

3. Reduction in the rate of material utilization and wastage by the economy.

It is, however, interesting to note that, in the past, many recovery methods proposed have been rejected because it is cheaper to dump the wastes than to process them. With stricter anti-pollution regulations and recovery processes making very good economic sense, pollution abatement through product recovery, either wholly or partially, should be promising in order that the natural resources of the country may be handed on to posterity undamaged and undestroyed.

Valuable by-products may include:

1. Water and other solvents for recycle.
2. A major product that is collectable in a commercial form, e.g., iron ore dust from blast furnace gas effluents.
3. A major product collectable in a non-commercial form, e.g., in dilute solution.
4. A saleable or presently useable by-product.
5. A by-product not presently an article of commerce.

Recycled water may ultimately be the major valuable product because of increasing water supply costs, increasing water treatment costs and mounting charges for using municipal sewerage facilities. As considerable work has been done and reported in the literature[1-12] on renovation and reuse of water, this subject will not be discussed. The recovery of product fines, useable water and thermal energy are important methods of reducing overall waste disposal costs and should be seriously considered in every case. Recovery of products from solid wastes is not included as it falls outside the scope of this report. There are many products that are recovered now but there are many more that are not being recovered now that could be recovered in the future by the so-called second generation recovery systems.

ECONOMIC, TECHNICAL AND PHILOSOPHICAL FRAMEWORK

The product of waste must be considered as an integral part of the manufacturing process and the cost of treatment of industrial wastes must be charged against the product. The waste disposal operations result in a net cost to the industry producing the waste, but product recovery and utilization practices reduce the cost of treatment and frequently prove to be cheaper than other methods of disposal.

While considering treatment of a waste, the choice of a method of treatment or process is made that gives maximum benefits or returns. In many cases, the industrial wastes contain valuable products such as high value metals, acids and other products which could be used for producing by-products and these, when recovered, will give high economic returns in addition to removal or pollution load from the waste stream. Further, in some cases, water recovered from these wastes are of good quality and can be reused, resulting in the reduction of waste and cost of treatment. The renovation and reuse of waste water becomes a necessity when the natural water supply source is limited and water needs are increasing, due to growing population and expanding industries.

By-product recovery frequently accompanies water reuse and water conservation. Recycled water may ultimately be the major valuable product because of increasing water supply costs, increasing water treatment costs, and mounting charges for using municipal sewerage facilities.

Industrial wastes contain toxic chemicals such as cyanide, free acids and heavy metals. Disposal of these wastes into surface waters are objectionable because they cause fish kills, retard self purification of surface waters. These wastes cannot be discharged into the sewage treatment plants as they contain toxic materials. The reduction of waste load is of major importance in the waste treatment operations. Waste load reduction is achieved by removing the spent grains in a semi-dry state, by removing the yeast from fermenters for filtration and drying and by removing the sediment from the chill storage tanks as a slurry for separate disposal. In many cases, these operations have yielded a saleable by-product which has more than offset the increased cost of recovery.

Frequently, waste streams can be eliminated or reduced by process modifications or improvements. A notable example of this is the use of save-rinse and spray-rinse tanks in plating lines. This measure brings about a substantial reduction in waste volume and frequently a net reduction in metal dragout.

Segregation of waste streams is a necessity at times, not from the product recovery point of view but from the operational point of view. An example of this is segregation of acidic metal rinses from cyanide streams to avoid the production of toxic hydrogen cyanide (HCN) and thus eliminate potential safety hazards.

From the industries' philosophical point of view, the prime requirement of waste treatment, by-product recovery and water reuse is that the principal product or products of the plant is satisfactory to the consumer and the secondary requirement is that the operation of the plants be efficient and economical.

The urgent problems facing the industries are how to recover by-products from waste materials inherent in every industrial operation and what to do with the by-products. Confronted with the growing dangers of air and water pollution, the anticipation of government regulation, as well as loss of valuable materials through unprofitable waste disposal methods, industries are forced to develop sophisticated refining methods for processing chemical and industrial by-products and even develop markets for by-products.

The industries, in general, are becoming more and more aware of the necessity for pollution abatement and product recovery, not only because of its effect upon the general welfare of the public, but also because of its own dependence upon rivers and streams for suitable water for manufacturing processes. Industries are also increasingly aware of the fact that benefits accruing from pollution abatement through product recovery may be quite significant.

PULP AND PAPER MILLS

Recovery of chemicals from cooking liquor and process water reuse are the two important efforts in the conservation and pollution control in this industry and the other efforts are recovery of by-products from spent liquor and bark.

The present status of recovery technology in this industry is shown in Figure 7.

Cooking liquor recovery was developed in order to reduce the cost for cooking chemicals and reduce the waste water load being discharged to stream. In the Kraft process of pulping, economic considerations dictate recovery and reuse of chemicals and, therefore, stream pollution from Kraft operation is less prevalent when compared to other types of pulping.

In the modern technology, liquor recovery system is an essential part of the pulping process and the recovery technique is different with each type of pulping method.

1. Kraft Liquor

   A major part of the chemicals in the spent cooking liquor (black liquor) is usually recovered in a series of operations: evaporation, burning and causticizing. The dissolved organic residues from the wood resins can be used for heat and power generation. Some soda is lost in the washing operation and, therefore, salt cake is added to the recovered liquor.

2. Sulfite Liquor

   Sulfite liquor recovery techniques are more complex and difficult than those employed in the sulfate system. In fact, the feasibility of liquor recovery is dependent on the base involved in the sulfite liquor. It is generally conceded that recovery is not practical with the calcium base. When a magnesium base is used, the spent liquor is evaporated and burned and chemicals recovered for reuse. However, for the sodium base, it is possible to recover the inorganic chemicals with a fairly complex process. Spent chemicals from the ammonium base sulfite pulping process can only be partially recovered but the process does not appear economically promising.

   Numerous products including Torula yeast and alcohols are produced from waste sulfite liquor by fermentation. Phenol may be produced by pyrolysis, vanillin by lime addition,

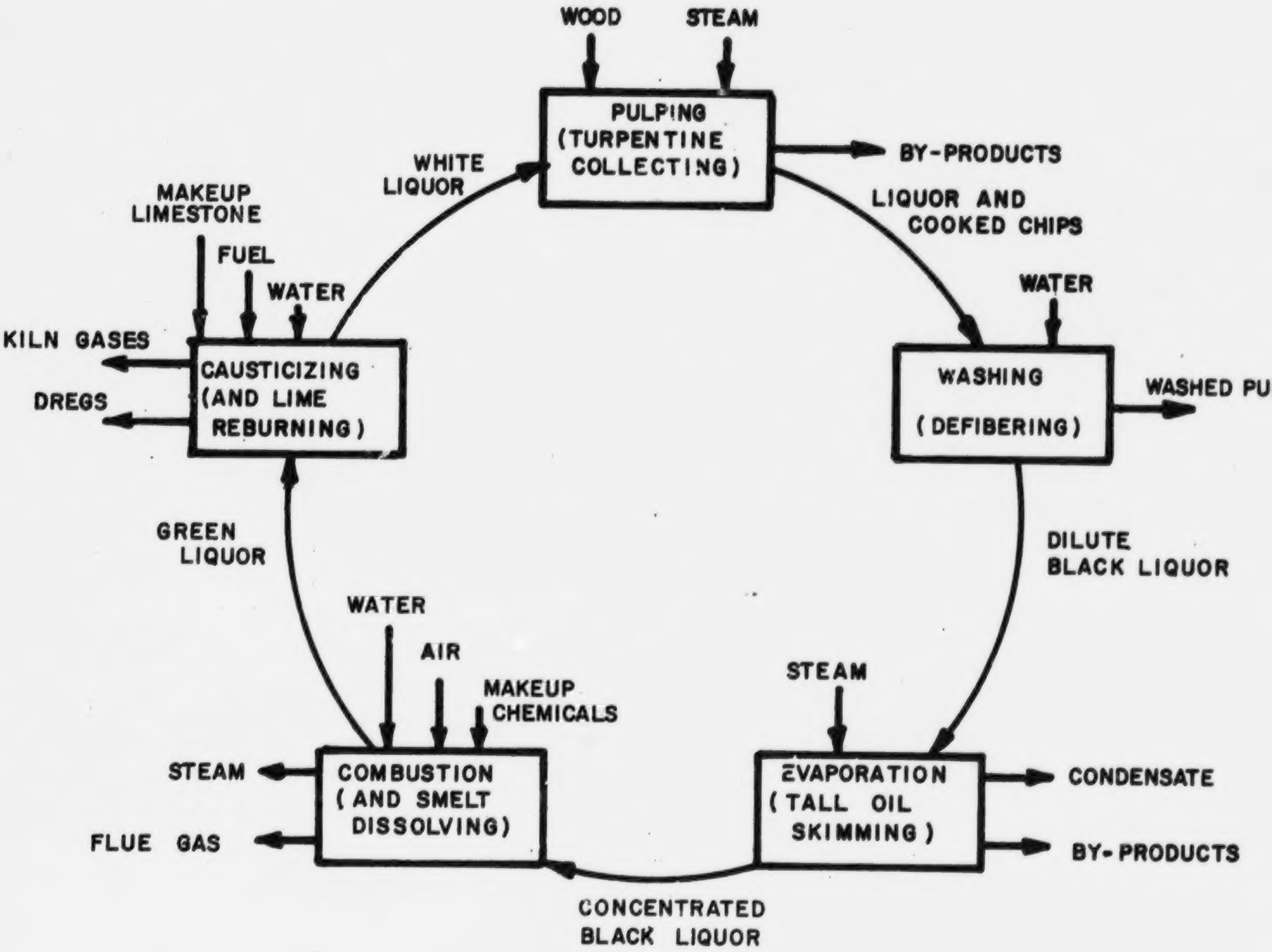
WOOD
STEAM
PULPING (TURPENTINE COLLECTING)
BY-PRODUCTS
WHITE LIQUOR
LIQUOR AND COOKED CHIPS
MAKEUP LIMESTONE
FUEL
WATER
WATER
KILN GASES
CAUSTICIZING (AND LIME REBURNING)
DREGS
WASHING (DEFIBERING)
WASHED PULP
GREEN LIQUOR
DILUTE BLACK LIQUOR
WATER
AIR
MAKEUP CHEMICALS
STEAM
STEAM
COMBUSTION (AND SMELT DISSOLVING)
FLUE GAS
EVAPORATION (TALL OIL SKIMMING)
CONDENSATE
BY-PRODUCTS
CONCENTRATED BLACK LIQUOR

FIGURE 7

PRESENT STATUS OF RECOVERY CYCLE

while acetic acid, formic acid, dimethyl sulfoxide (DMSO) and lignosulfonates are recoverable directly.

3. Semi-chemical Liquor

Liquor recovery in the NSSC (Neutral Sulfite Semi Chemical) process is practiced in some independent NSSC pulp mills using a complicated carbonation method. In the integrated semi-chemical Kraft mills, the recovery system is also integrated. The "cross recovery" method is based on the sodium and sulfur values in the NSSC liquor that can be used as chemical make-up in place of salt cake. The NSSC spent liquor can be combined with Kraft liquor for evaporation and combustion but the NSSC cooking liquor has to be made from fresh chemicals.

The KSC spent liquor is recovered in the same process that is used in a regular Kraft pulping process.

Large quantities of water are essential in the pulp and paper manufacturing processes such as pulp processing, washing, dissolving or mixing the various loading, sizing, and color ingredients, and carrying the fibers through the screens and refiners to the paper-making machine. Water is also used to convey by-products and undesirable wastes and to generate power and steam. The maximum reuse of water becomes one of the basic approaches in the effective reduction of waste water quantities.

There are definite limits in the amount of mill water which can effectively be reclaimed and reused. Fresh water has to be added in certain operations to prevent the build-up of undesirable dissolved solids, temperatures, and slime from bacteria and fungi growth.

Each mill has its own approach on how best to reuse water in the various operations. However, the following process waters are most frequently collected and reused:

1. Water from the log flumes and barkers.
2. Evaporator condensate from the liquor recovery area.
3. Bleach plant washer filtrate.
4. White water from the paper machine.
5. Washer water from coarse screens.

An accepted practice is the reuse of waste water in wood handling and storage such as in the log flumes, hot pond, hydraulic or wet drum debarker, and for the showers prior to chipping. For these applications, heated effluents discharged from evaporators, bleach plant, or paper machine are preferred because the heat increases bark removal efficiency. Recycling barker effluent, which has been cleaned and screened, is a widely practiced water reuse procedure.

In the pulp mill, the waste water from the digester usually contains the spent cooking liquor and the condensate from the digester heat exchanger. If the cooking liquor is recoverable, the water is evaporated and collected as condensate while chemicals are recovered for reuse. The condensate collected is used in steam generation, as scrubber water for flue gas or in the brown stock washing process.

In the screening department, a large amount of waste effluent may be reused as dilution water ahead of the screening and cleaning operation. However, since the washing operation is intended to remove the cooking liquor from the pulp, economics dictate that a considerable amount of the contaminated wash water be displaced by make-up water since this reduces the pulp's chlorine demand in a later operation and also prevents the build-up of dissolved solids which cause salting out and foaming on the screens. The necessary make-up water is obtained by reusing the pulp mill condensate, condenser cooling water, paper machine white water and certain bleach plant filtrates.

In the Kraft chemical recovery process, water can be reused in the following operations:

1. Dregs washing.

2. Green liquor dilution.

3. Lime slaking, lime mud washing and lime kiln scrubbing.

4. White liquor filter back washing.

5. Scrubbing of flue gases.

The primary source of water to be reused in these processes is the evaporator condensate.

In the sulfite chemical recovery process, the evaporator condensate is used to dilute the soda ash from the furnace and to scrub the flue gases when recovering SO_2. The washing of the bleached pulp and removal of the residue lignin requires a large amount of water. The waste waters generated contain a large amount of color and have a tendency to foam requiring fresh water make-up. The amount of fresh water make-up required can be reduced by employing the following water reuse techniques:

1. The use of washer filtrate for dilution of stock leaving the bleaching towers.

2. The use of excess washer seal box waters in the preceding seal box washing cycle.

3. The use of white water and excess cooling water to dilute the finished bleached pulp.

4. The use of digester condensate for shower water, bleaching tower dilution water and known stock dilution water.

The estimated percentage of the total process water reused in the paper and pulp industry is in the range of 63 - 73%.

The installation of save-alls in paper mills to recover fiber permits the reuse of treated water. When a disk filter is employed, the cloudy filtrate is returned to the pulpers as make-up water and the clear filtrate is used for many purposes. The overflow is discharged to the sewer. The use of flotation save-all also results in a similar operation. A simplified scheme of two pulp and fiber recovery systems in a paperboard mill is shown in Figure 8.

Reverse osmosis is finding its potential use for the recovery of demineralized water and concentrating the solutes from pulp mill effluents.

Deinking sludge solids contain 50 - 75% clay and these are particularly useful in the following applications:

1. Light-weight aggregate for building blocks.

2. Filler for asphalt tile and liquid emulsions.

3. Filler for fiberboard and other lined board.

4. Filler for paper, rubber and other manufacturing materials.

Recovery of lime at a recovery rate as high as 97% from causticizing operations in the Kraft wood-pulping process[13] has been practiced with advantage. The recovery process consisted of dewatering on vacuum filters and calcining the concentrated slurry in a 1600° F. kiln.

Several organic by-products can be and are being recovered from the spent cooking liquor resulting from various types of pulping operations. They include turpentine, tall oil, yeast, alcohols, dimethyl sulfoxide, vanillin, etc.

Digester relief gases from both sulfate and sulfite pulping contain significant quantities of turpentine. The turpentine recovery procedure consists of condensing the cooking relief and decanting the crude oil fractions. The turpentine is used as paint thinners and in the manufacturing of insecticides. Yields vary from 1.5 to 4.3 gallons/ton of pulp.

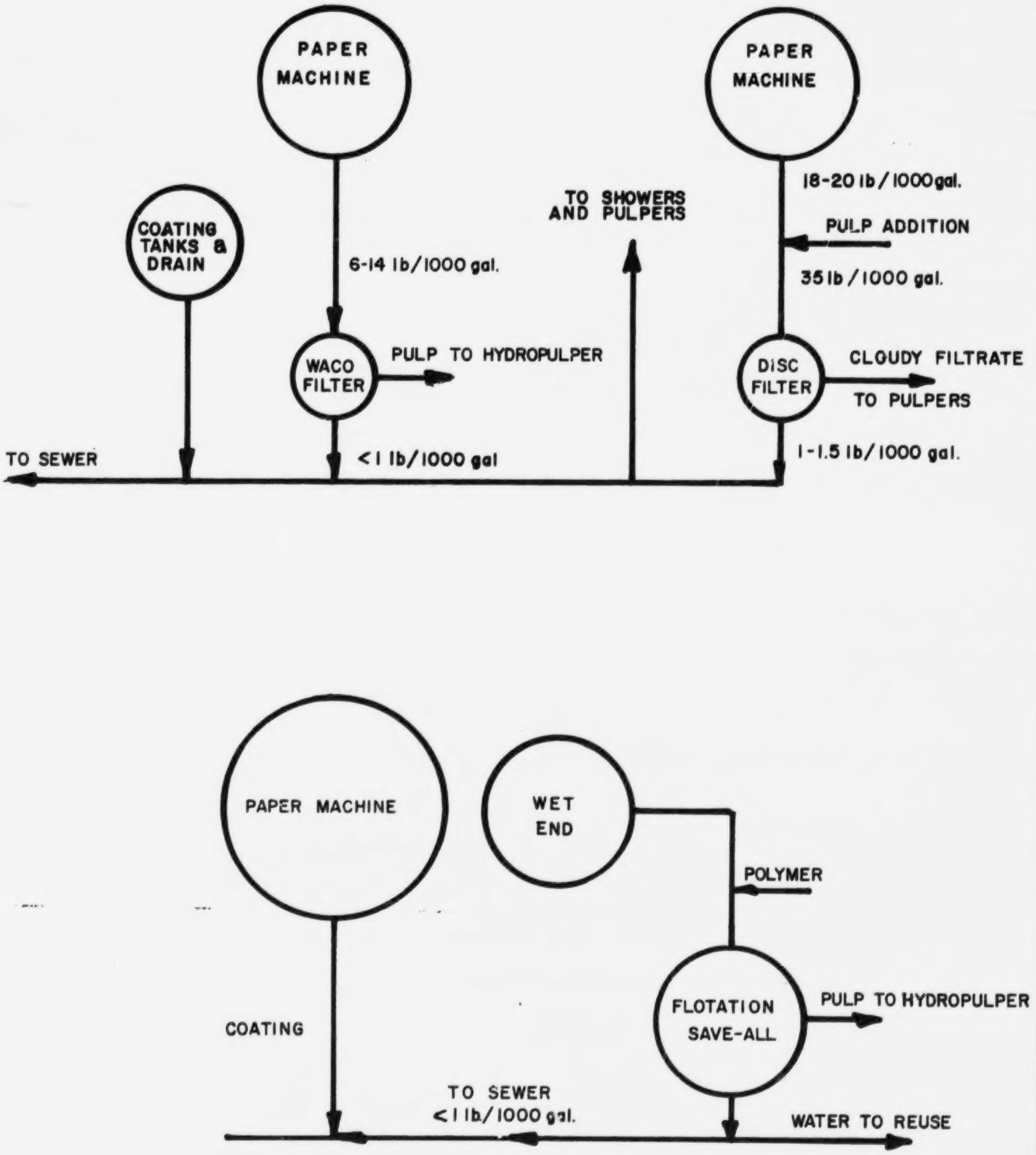
PAPER MACHINE
PAPER MACHINE
COATING TANKS & DRAIN
6-14 lb/1000 gal.
TO SHOWERS AND PULPERS
18-20 lb/1000 gal.
PULP ADDITION
35 lb/1000 gal.
WACO FILTER
PULP TO HYDROPULPER
DISC FILTER
CLOUDY FILTRATE TO PULPERS
TO SEWER
<1 lb/1000 gal
1-1.5 lb/1000 gal.
PAPER MACHINE
WET END
POLYMER
FLOTATION SAVE-ALL
PULP TO HYDROPULPER
COATING
TO SEWER <1 lb/1000 gal.
WATER TO REUSE

FIGURE 8 PULP AND FIBER RECOVERY IN A BOARD MILL

Tall oil is recovered from the black liquor by various refining operations and the yields are 180 - 300 lb/ton of dry pulp. Tall oil and its derivatives are used to make adhesives, emulsions, disinfectants, lubricants, paints and soap.

Torula yeast is produced from spent sulfite liquor by fermentation. Torula yeast contains large amounts of proteins and vitamins and it is used as a food supplement for humans and animals. Waste reduction resulting from yeast production is about 95% for total solids, 20% for BOD's, and 60% for total waste water volume.

Alcohols are attained as by-products in the fermentation of spent sulfite liquor by using specific yeast organisms. Ethyl alcohol is produced as a first-stage product and can be further processed to produce glycols, ethyl acetate, ethylene dichloride and acetaldehyde.

Dimethyl sulfoxide (DMSO) is a valuable compound extracted by a series of complicated processes from liquor dissolved in spent cooking liquor. DMSO can be used as an antiflammatory agent or as a bactericide.

Vanillin is generated from the calcium-base sulfite spent liquor by treatment of calcium lignosulphonate with sodium hydroxide under pressure.

It has been established that bark from particular trees can be used as a source of a saleable by-product while many types of bark can be used directly in the manufacture of roofing felts, thermal insulation materials and cheap wrapping paper. By-product utilization of bark is currently being studied intensively by the industry.

Many other by-products can be and are being generated from the sulfite spent liquor. These include emulsions for insecticides, scaling inhibitors for boilers, tanning agents, cement dispersing agents, fertilizers, flotation acids for separation of ores, well drilling lubricants, extenders in storage batteries, reinforcing agents for rubber, gradients for ceramic industry electroplating and road binders.

In spite of the numerous fields in which the spent sulfite liquor can be utilized, the amount actually used is very small. The prospect of finding an economical use of waste liquor is questionable at the present technological level in large part because cheaper and better raw materials for making these products are available.

There are various miscellaneous processes and modifications of conventional processes related to product recovery that are worth reporting.

There is a new process applicable to all acid or alkaline base pulps that offers substantial savings[14]. The flue gas obtained by burning the concentrated spent liquor gives up its heat to the incoming dilute spent liquor in direct contact, supplying energy for evaporation of the dilute liquor. Then the flue gas is scrubbed to recover chemical values (thereby forestalling air pollution problems) as well as additional heat. This method contrasts with conventional processes wherein flue gas heat is used to produce steam and the steam, in turn, heats the evaporators. By eliminating the steam boiler and steam evaporator, the new approach cuts the required liquor handling investment by about one half.

Nuclear irradiation of gases produced at Kraft pulp mills was found successful to make them less objectionable[15]; also, irradiation of sulfite-mill water pollutants was found to modify their water solubility and make them easier to treat. Similar studies involving sewage and liquid industrial wastes are being made by the Metropolitan Sanitary District of Chicago.

In the Kraft pulping process, the burning of spent liquor is a necessary step to recover heat and chemicals. This process releases dust and sulfur-bearing gases into the air. Using a Venturi scrubbing system[16], 99% of the dust is removed from flue gases and an improved oxidation step greatly reduces the amount of H_2S released to the atmosphere.

A new selective hydrogenation process[17] for pulping wood and other cellulosic materials patented by Pressure Chemical Company (Pittsburgh) converts more than 90% of the wood feed, including ligneous portions, into useable pulp. This high rate of conversion has other advantages in addition to minimizing the stream pollution; they are as follows:

1. Water is used as a solvent instead of the organics.

2. The organo metallics used for catalysis can be recovered and recycled.

3. Hydrogen consumption is low because there is no appreciable cleavage of carbon bond.

The limitations of this process are that the dry pulp produced has to be bleached and cannot be fed directly to an ordinary Fourdrinier paper-making machine.

A radically new process[18], "Holopulping", developed by the Institute of Paper Chemistry (IPC), slashes the cost of chemicals to pulpers by two-thirds and increases the yield by 20 to 30%. It eliminates the use of sulfur and regenerates its basic pulping chemicals and, compared to the Kraft process, greatly reduces pollution. Holopulping is a selective delignification process and the process is shown in Figure 9.

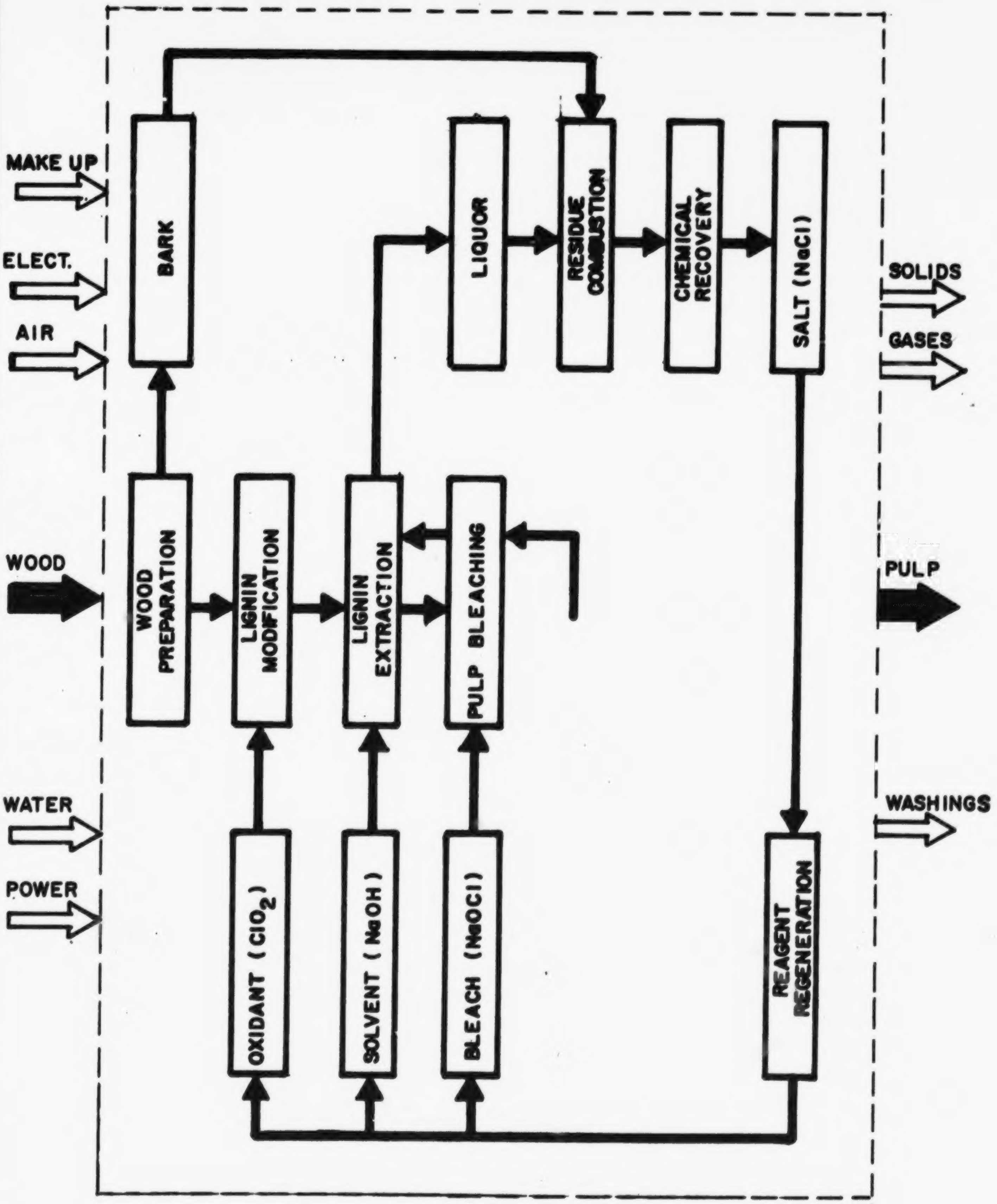
MAKE UP
ELECT.
AIR
WOOD
WATER
POWER
BARK
WOOD PREPARATION
LIGNIN MODIFICATION
LIGNIN EXTRACTION
PULP BLEACHING
LIQUOR
RESIDUE COMBUSTION
CHEMICAL RECOVERY
SALT (NaCl)
OXIDANT (ClO2)
SOLVENT (NaOH)
BLEACH (NaOCl)
REAGENT REGENERATION
SOLIDS
GASES
PULP
WASHINGS

FIGURE 9
HOLOPULPING PROCESS

The other major features are:

1. Chemical regeneration and recycle is relatively simple. The pulping and bleaching liquors are of similar chemical nature and they can be treated in a single stream. Also, the recovery of products is generally very efficient and the products can be used in the pulping operations.

2. Stream pollution is kept at a minimum by countercurrent washing. The remaining calcium sludge waste is disposed of without causing harmful effects. Air pollution is greatly reduced because the organic materials are burned and few odorous compounds are formed.

3. The process may mean a loss of markets for the chemical industries but the advantage of holopulping is in the conservation of forest resources and natural environments by producing more pulp with a smaller amount of chemicals at the expense of electric energy.

In a hard-board mill[19], the soluble sugar in the pulp washer water is concentrated in evaporators in stages to recover "Masonex" - a molasses type cattle feed - as a by-product. This product is said to have a worldwide market as a food supplement carbohydrate or pellet binder.

The fluidized bed processing has been applied to spent sulfite liquor combustion by Dorr-Oliver[20] and was found to present an economical solution to both water and air pollution abatement by converting the spent liquor to a granular inorganic solid and a clean, dust free, odorless exhaust gas. In most cases, complete or partial chemical recovery is possible or a saleable product is produced so that the operating costs associated with the operation can be offset. Even more attractive is the fact that when chemical recovery is coupled with other recovery devices, as high and low level heat recovery, return on investment becomes an attainable asset.

Hydrogenation of waste liquor containing lignin yields a multitude of products[21], but only phenol offers an attractive combination of price and market volume. The solids concentration is 10% by weight and is concentrated to 50% before feeding the liquor to the hydrogenation lignin reactor. The products from organic lignin are as follows:

Products	Yield, % by wt. of organic lignin
C_5 - hydrocarbons	19.5
Neutrals	14.0
Phenols	37.5
Catechols	8.7
Bottoms	2.4
Water and others	23.6

The neutral and organic liquid products are given a by-product value of 1¢/pound. Additional credits are available from the conversion of sugars. The bottom material is given a value of 21¢ per million BTU, a very low value for fuel. The recovered ammonia is valued at $30/ton.

Hydrogenation can be effectively used for the bleaching of wood pulp and conversion of cellulosic structures to poly-hydroxyl organic compounds of lower molecular weight by hydrocracking seems an intriguing possibility.

Table I summarizes by-product recovery in the pulp and paper mill industries.

TABLE I

BY-PRODUCT RECOVERY IN THE PULP AND PAPER MILL INDUSTRIES

	By-Product Recovery			
Process	By-Product	Quantity	Value - Recovered Products	Diminution of Pollutional Load
Kraft	Turpentine	1.5-4.3 gal/ton	$0.20-0.40/ton	1%
	Tall oil	180-300 lbs/ton	$9-15/ton	2%
	Lime	2.0 tons/ton	$40/ton	95%
	Soda ash	1.5 tons/ton	$40/ton	95%
	Fiber recovery	Not relevant		20-70%
Sulfite	Torula yeast	500 lbs/ton	$25/ton	90%
	Various alcohols			
	Lignosulphonates	1500 lbs/ton	---	70%
	DMSO		$10/ton	1%
	Vanillin	500 lbs/ton	$40/ton	90%
	Phenol			
	Acetic acid	30 lbs/ton	$3/ton	4%
	Formic acid	8 lbs/ton	$0.80/ton	1%
	Fiber recovery	Not relevant		
NSSC	See Kraft and Sulfite Processing			
Debarking operations	Bark	100 lbs/ton	$100/ton	10%
Holo-pulping	Sodium hydroxide	Quantities not confirmed in full test.		

STEEL INDUSTRY

The disposal of waste pickle liquor is a major problem that has been plaguing the steel industry. The steel companies frequently find it costs almost as much to dispose of the waste as it does to buy the acid.

There are various methods for treatment, disposal and product recovery for pickle liquors such as lime neutralization, evaporation-crystallization, controlled neutralization, electrolysis and dialysis. Lime neutralization, though very commonly used, is an expensive method without any product recovery. When evaporation-crystallization is practiced, only free acid amounting to half the requirement for pickling is recovered. Further, even though the cost of evaporation-crystallization is not excessive, the disposal of ferrous sulfate ($FeSO_4$) poses further problems because of its inadequate market. Electrolytic schemes for complete acid recovery and plating metallic iron are being used with advantage.

Controlled neutralization with lime (duPont process) produces a smaller volume of sludge and easy to dewater solids[22]. Magnetic iron oxide formed is easily recoverable and crystalline gypsum may be used for wallboard or cement manufacture. If local conditions do not justify recovery, solids may be piled as land fill.

Recovery of sulfuric acid and iron from waste pickle liquor in the steel industry has been technically proved feasible in the Ruthner process[23]. This recovery system is a non-paying one with high investment. Roasting of ferrous sulfate monohydrate (crystallized from pickle liquor) with carbon and air to produce iron oxide and sulfur dioxide has been proposed. On a large scale, this system appeared more economical than the Ruthner process. The acid produced here would be shipped back to the steel mills or other customers. Iron oxide, to be of value, would have to be sintered and shipped back to the mills. Sulfuric acid recovered is the only significant credit here and recovery of iron in a ready-to-melt form, rather than iron oxide, is very desirable.

Several electrolytic schemes have been proposed in the past to plate metallic iron from waste pickle liquor and one such scheme with high efficiency of iron plating and acid formation is shown in Figure 10.

Evaporation-crystallization has been used in producing ferrous sulfate crystals and the flow sheet is shown in Figure 11. Waste pickle liquor is evaporated at 160° F. and ferrous sulfate is then crystallized in a vacuum crystallizer and cooled down to 30° F. The crystals are separated from the mother liquor by centrifugation. The mother liquor is diluted to 25% acid, thereby reducing the

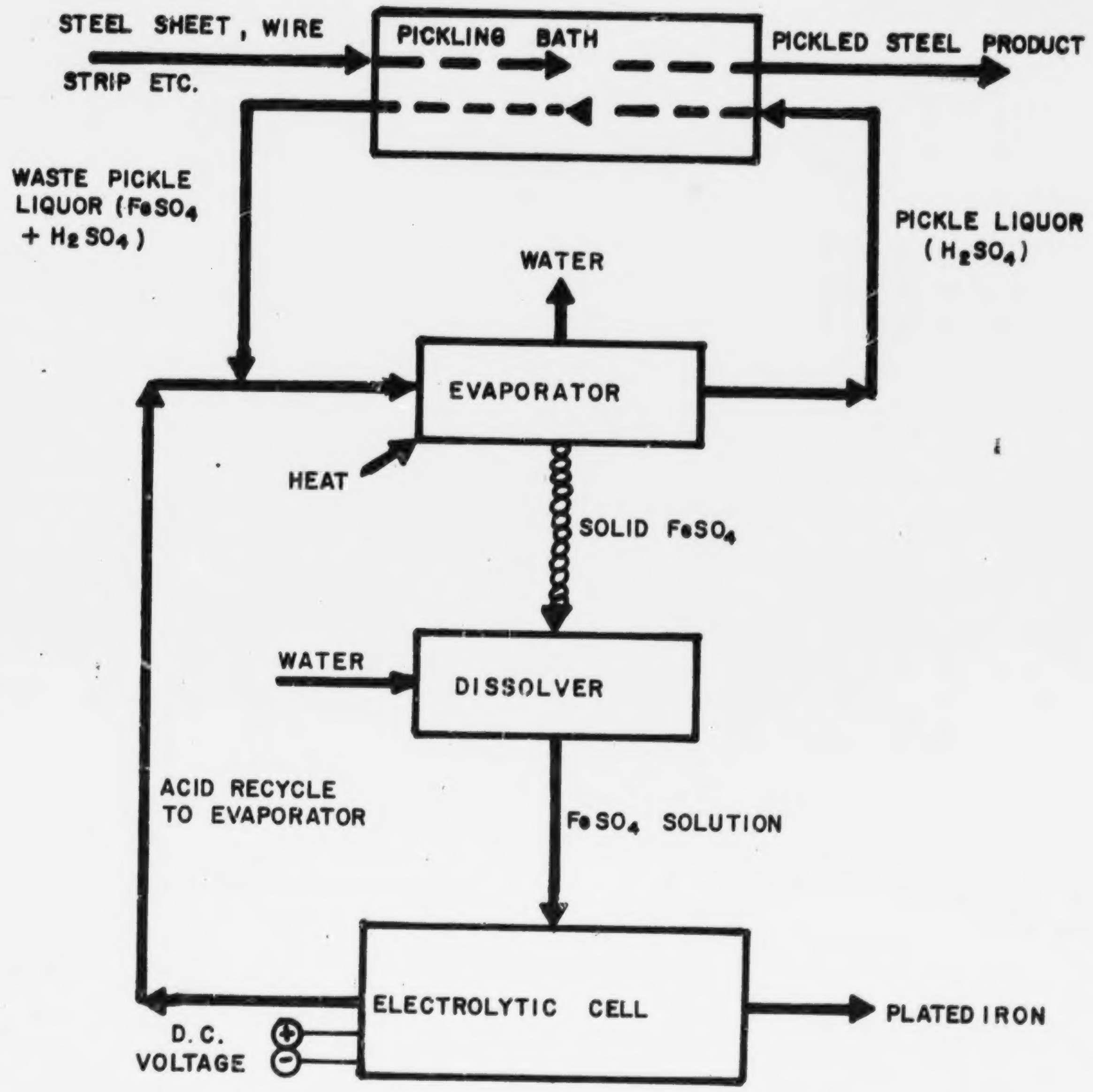
STEEL SHEET, WIRE
STRIP ETC.
PICKLING BATH
PICKLED STEEL PRODUCT
WASTE PICKLE LIQUOR ($FeSO_4$ + H_2SO_4)
PICKLE LIQUOR (H_2SO_4)
WATER
EVAPORATOR
HEAT
SOLID $FeSO_4$
WATER
DISSOLVER
ACID RECYCLE TO EVAPORATOR
$FeSO_4$ SOLUTION
ELECTROLYTIC CELL
PLATED IRON
D.C. VOLTAGE
+
−

FIGURE 10

RECOVERY OF SULFURIC ACID AND IRON FROM WASTE PICKLE LIQUOR IN THE STEEL INDUSTRY

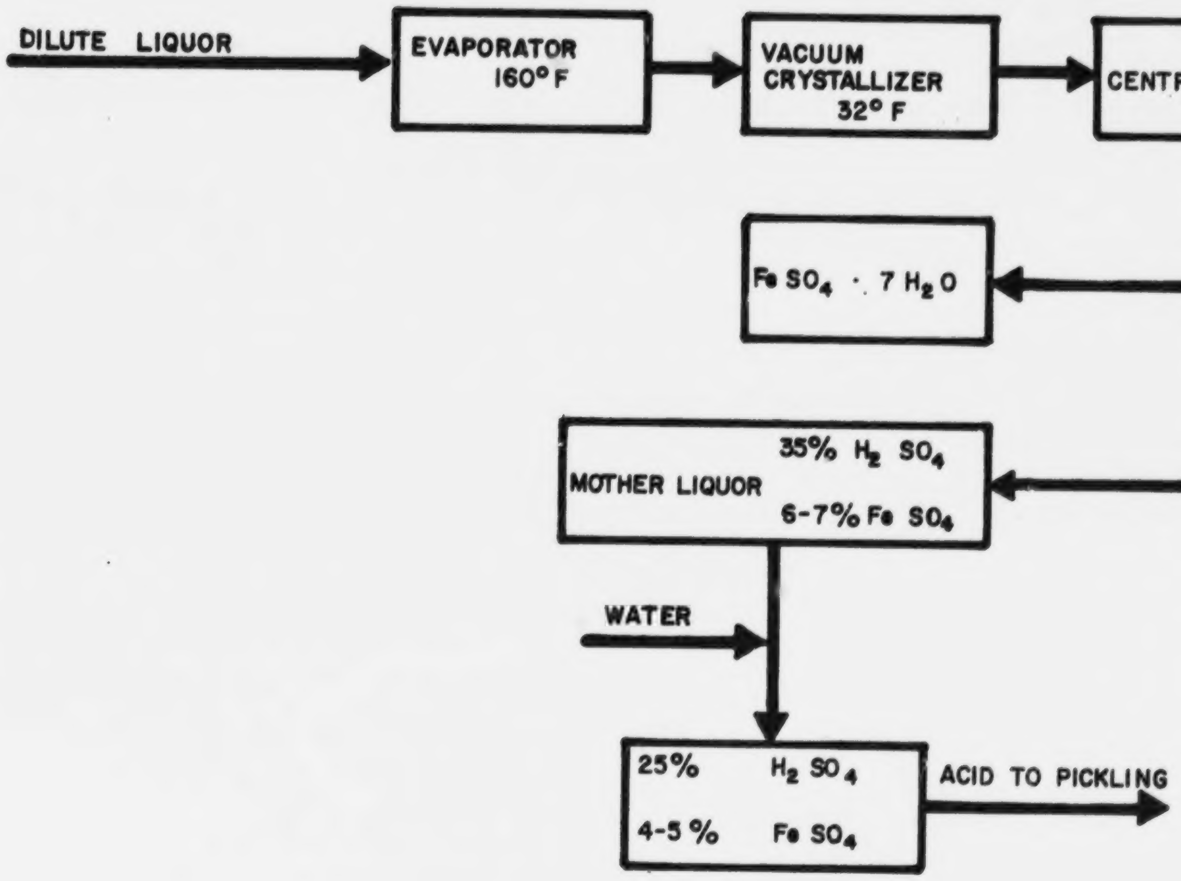
DILUTE LIQUOR
EVAPORATOR 160° F
VACUUM CRYSTALLIZER 32° F
CENTRIFUGE
$FeSO_4 \cdot 7H_2O$
MOTHER LIQUOR
35% H_2SO_4
6-7% $FeSO_4$
WATER
25% H_2SO_4
4-5% $FeSO_4$
ACID TO PICKLING

FIGURE 11

EVAPORATION– CRYSTALLIZATION ($FeSO_4 - 7H_2O$)

(S. A. LAURICK – STRUTHERS – WELLS CORP) residual ferrous sulfate to 4.5% and this solution is returned to pickling.

Dialysis, a separation process utilizing diffusion as its driving force, may be used for the economical recovery of acids[24]. In the viscose rayon industry, dialysis provided the means for recovering the bulk of the wasted caustic soda. About 0.85 pounds of caustic were recovered per pound of rayon produced, sufficient to have a real effect on the production cost. Recovery of sulfuric acid was done in two copper refineries on full scale plant units. The economic feasibility of dialysis for stainless steel pickle baths has also been proven.

Dialysis is a simple unit operation requiring a minimum of operator attention. The operating cost is almost nil as no power or chemical is used. However, it should be noted that dialysis alone will not resolve a waste treatment problem, but its role to remove raw materials and to reduce plant waste is significant. Some acid systems may allow recovery of as much as 70 or 75% of currently wasted acid, but even recovery of as little as 20% of the wasted acid may justify the process from the economical point of view.

The pickling of steel in the United States is predominantly done with sulfuric acid. The acid used is consumed and produces a waste pickle liquor which is both uneconomical and extremely difficult to regenerate. The waste pickle liquor is normally neutralized and/or dumped. This method of disposal is becoming more and more difficult to pursue. A practical answer to this problem is the use of hydrochloric acid instead of sulfuric in the pickling operation. Major steel strip manufacturers in the United States have already started the trend[25] toward hydrochloric acid due to the following reasons:

1. Hydrochloric acid prices are dropping while sulfuric acid prices are rising.

2. Hydrochloric acid pickling is faster and produces a better quality product.

3. Most importantly, hydrochloric acid waste pickle liquor can be and is being regenerated economically.

Switching to hydrochloric acid is not practical in the open-batch pickling of wire, pipe and plate due to the production of corrosive vapor. In the continuous strip pickling operations where hoods and ventilation systems are provided, the switching is relatively easy. The vapor problem has been avoided in Europe by using enclosed tunnel and Ottoclave picklers.

The handling of spent pickle liquor is done by the Turbulator process[26]. The turbulator process simply reverses the reaction that occurs in the pickling bath and, thereby, regenerating the hydrochloric acid and iron oxide consumed in operation.

$$2FeO + 4HCl \longrightarrow 2FeCl_2 + 2H_2O$$

$$2FeCl_2 + 2H_2O + \frac{1}{2} O_2 \longrightarrow Fe_2O_3 + 4HCl$$

The pickling-regeneration cycle can also be symbolized as shown in Figure 12.

Theoretically, all the hydrochloric acid is recovered in this cyclical system. In practice, however, some loss does occur in the pickling and regeneration process which makes it necessary to add a small amount of fresh acid to the pickling system. The advantages of the turbulator process are as follows:

1. High reaction rates resulting in small space requirements.

2. High operating flexibility in very short start-up and shut-down times.

3. Low maintenance requirements.

4. A system that can point to actual operating plants.

In a process developed by Interlake Steel Company--duPont[27], waste hydrochloric acid pickle liquor is neutralized and discharged rather than regenerated. In the process treating 11 million gallons per year of acid waste, pickle liquor (spent HCl, $FeCl_2$ and water) is neutralized by adding lime and ferrous hydroxide $[Fe(OH)_2]$ and calcium chloride ($CaCl_2$) are formed. The ferrous hydroxide is oxidized to magnetite (Fe_3O_4) and separated from weak calcium chloride solution, sintered and returned to furnace. Recovery will be 5000 ton/year from waste liquor. Calcium chloride is usually diluted and discharged into sewers or natural waters but it could be recovered by concentration.

Because of the relationship between hydrochloric acid, pickling and regeneration as a natural complement to the other, it is believed that the use of hydrogen chloride in the pickling operation will play a large part in the future[27]. Presently in the United States, Dravo Corporation accomplishes hydrogen chloride regeneration in a spray roaster and in Germany, Lurgi has developed a fluid bed acid regeneration process.

The elimination of phenol (C_6H_5OH) from coke plant ammonia liquor has been a problem of major concern to the steel industry. Solvent extraction process was found to have possibilities of attaining the advantages such as high efficiency, operating charges as low as possible and lowest investment. In the solvent extraction process[28], raw

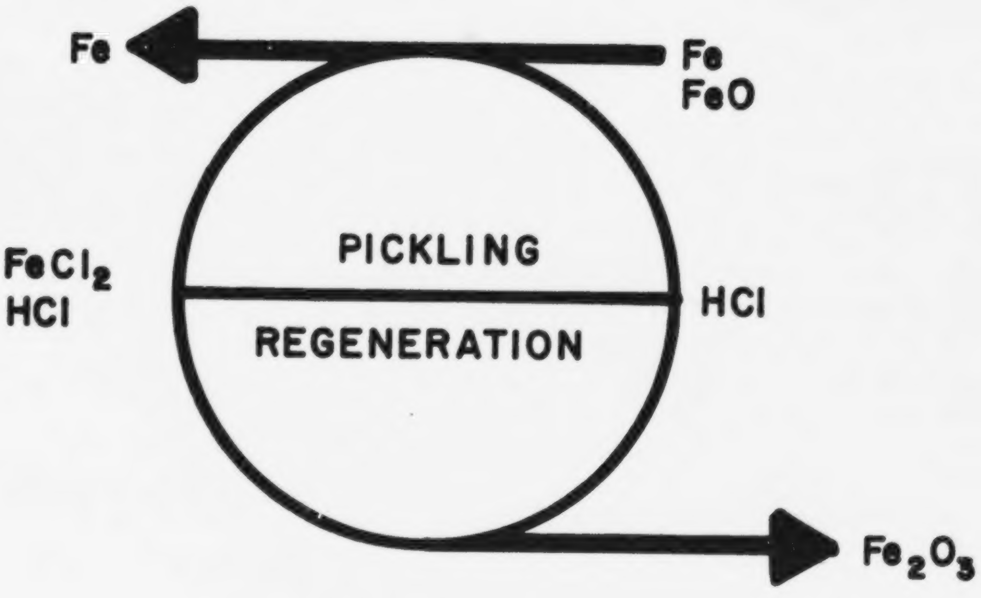
Fe
Fe
FeO
PICKLING
FeCl2
HCl
HCl
REGENERATION
Fe2O3

FIGURE 12
PICKLING REGENERATION CYCLE

ammonia liquor is contacted countercurrently with a solvent, such as light oil, readily available in the coke plant. The solvent removes the phenol and, in turn, is treated with a caustic soda solution for extraction of phenol as sodium phenolate (C_6H_5-ONa), and then the solvent is recycled. The caustic concentration greatly influenced the percentage of elimination of phenol from the liquor. The more dilute caustic used, the better the phenol elimination. A phenolate of reasonable concentration must be produced to be saleable. This was achieved by employing two streams of caustic of different strengths as feeds to the reactor; the desired elimination of phenol and concentration of product could be obtained. The removal efficiency for phenol was reported to be about 98%. Ammonium sulfate is regularly recovered from these waste waters by neutralization with sulfuric acid and crystallization of the salt.

A new process developed in Japan[29] turns pyrite (FeS_2) cinder into pellets with a high iron content, suitable for feeding to blast furnaces. This increases the iron ore requirements as Japan develops only about 10% of iron ore requirements domestically from sources such as pyrite float concentrates. Process economics are improved by the recovery and sale of precious metals contained in the cinder. Gas produced is treated by a wet system to recover Cu, Zn, Au, Ag and Pb. Other main features include:

1. Purification and pelletizing are done simultaneously.

2. The removal rates of copper, zinc and bismuth are higher than the conventional chlordizing, roasting and bleaching process.

3. Recovery rate for silver, gold is better.

4. Residual sulfur dioxide is recovered from the gas as gypsum.

In a grey iron foundry[30], briquetting was practiced to recover flue dust and mill scale and this process can be used to save a variety of valuable waste materials. In the steel industry, better use of turnings and borings left over in mill operations as scrap is made by making briquettes out of this scrap material and returning them to make more iron.

Table II summarizes by-product recovery in the iron and steel industries.

TABLE II

BY-PRODUCT RECOVERY IN THE IRON AND STEEL INDUSTRIES

	By-Product Recovery			
Process	By-Product	Quantity	Value	Diminution of Pollutional Load
Pickle liquor	Iron oxide	25-35 lb/ton	$0.10-0.20/ton	100%
	Gypsum	40-50 lb/ton	$0.10-0.20/ton	100%
	Sulfuric acid	30-40 lb/ton	$0.60-0.80/ton	100%
	Hydrochloric acid	30-40 lb/ton	$0.60-0.80/ton	100%
Grey iron foundry	Flue dust Mill scale	---	---	60-80%
Blast furnace scrubber waters	Mill scale	25-50 lb/ton		60-80%

PLATING AND ALLIED INDUSTRIES

The rinse water from plating industry mostly contains some or many of the following contaminants usually in intolerable amounts: hexavalent chromium, sodium cyanide, complex cyanides of the heavy metals, such as cadmium, copper, zinc, sometimes silver and gold, soluble nickel salts, strong mineral acids and strong alkalis. Of these, the most toxic are hexavalent chromium and the cyanide ion. Aquatic life is also sensitive to salts of the heavy metals.

There are several basic methods of treating this waste for final disposal or recovery of products. The oldest is the batch treatment method. In this method, the rinse waters are collected for treatment and disposal. The destruction of toxic chemicals is accomplished by oxidation of the cyanides and reduction of chrome. Chlorine (Cl_2) is used to destroy cyanides (CN) and the chlorinated rinse water is pumped into a reduction tank containing sulfuric acid and a reductant-like ferrous sulfate ($FeSO_4$), sodium bisulfite ($NaHSO_3$) or sulfur dioxide (SO_2). Chromium is reduced from its hexavalent state (Cr^{+6}) to trivalent state (Cr^{+3}) and is precipitated along with metals as their hydroxides by the addition of lime. The clear water from the clarifier would be ready for discharge into a sewer and the sludge is disposed by any convenient method.

Another method of treatment of rinse water is the continuous flow method. To be effective and fool-proof, this requires excellent instrumentation to monitor the flow and deliver the proper amount of reactant. Also, such a system may not allow enough reaction time to allow slow reactions to go to completion.

Where the volume of chromic acid and sodium or potassium cyanide used in the industry is great enough, the system of recovery of the cyanides and chromic acid by ion-exchange and evaporation has obvious economic advantages. However, when the plating operation is split up into several small, different operations involving chrome plating, several different kinds of chromating baths and several types of cyanide baths, this method becomes practical[31].

Lancy's integrated system of treatment of cyanide and chromium wastes is found to be suitable for a plating operation split up into several operations. The system involves countercurrent rinsing and the basic advantage of this system is that the toxic contaminants are destroyed before they can enter into the rinse water, rather than having to be removed later.

When reclamation of chemicals is desired, ion exchange plays an important role. The rinse waters are kept separate in the following categories:

1. Hard chrome rinse waters

2. Cyanide rinse waters containing silver, gold or any other valuable metal.

3. Miscellaneous wastes such as alkaline cleaners and acids.

The hard chrome rinse waters are passed through a cation and a strong base anion exchanger. The contaminating metals such as copper, nickel and trivalent chrome are exchanged on the cation exchanger, while the hexavalent chrome is exchanged on the anion exchanger. Upon exhaustion of the system, the cation exchanger is regenerated with an acid and the anion exchanger regenerated with caustic soda.

The regenerant effluent from the cation exchanger can be discharged to a collection chamber for neutralization. The regenerant effluent from the anion exchanger will contain sodium chromate and some caustic soda. This material can then be converted to chromic acid by passing back through the cation exchanger so that the two exchangers may be alternated between service and conversion.

The ion exchange system for silver recovery[32] would consist of a strongly acidic sulfonic cation exchanger and a strong base anion exchanger. The effluent from the system is de-ionized water and can be reused in the rinsing operation. Sodium hydroxide is used as a regenerant and the regenerant effluent contains sodium cyanide (NaCH) and sodium hydroxide (NaOH). This solution is passed downflow through the exhausted bed of the cation exchanger. The cation exchanger effluent contains sodium silver cyanide and NaOH. This regenerant solution may be used in the make-up of silver bath. Otherwise, addition of 15% sodium hypochlorite (NaOCl) solution precipitates the silver as silver chloride (AgCl) and destroys the cyanides. The AgCl is recovered and the supernatant liquid dumped in the sewer, cyanide free. Sodium silver cyanide can be recovered by this method for a chemical cost of approximately 18¢/pound of silver recovered.

The rinse water from gold plating line contains enough gold to make recovery economical[32]. The recovery of gold is accomplished by passing the rinse water through a strong base anion exchanger of the hydroxide form. After exhaustion of the resin, the gold is recovered by burning the resin. The residue remaining is metallic gold. One cubic foot of anion exchange resin, when exhausted with gold cyanide, contains approximately 125 ounces or $4,000 worth of gold.

The rinse water in the platinum plating industry contains platinum in the form of chlorophatinic acid. Strongly basic anion exchanger is used and when the resin is saturated with platinum, the recovery is achieved by burning the resin[32].

Nickel may be recovered from plating rinse waters by employing a cation exchange process[32]. The effluent from the service cycle of the hydrogen exchanger can be passed through a weak base anion exchanger to obtain deionized water for plant use. Sulfuric acid is used for regeneration and the nickel is eluted from the resin as nickel sulfate. The capacity of the cation resin is 5.0 pounds of nickel per cubic foot as nickel sulfate and the chemical cost for the process would be 20¢/pound of nickel sulfate recovered.

Brightening of aluminum is done by the use of concentrated phosphoric acid (H_3PO_4) and a small amount of nitric acid (HNO_3). Rinse water from this operation contains aluminum and dilute H_3PO_4. It is estimated in an industry in Illinois[33] that two to three million pounds of H_3PO_4 were lost each year. Cation exchanger was used to remove aluminum and the aluminum-free solution is evaporated in a multiple effect evaporator to obtain concentrated H_3PO_4 (85%) and good quality condensate. The recovery of H_3PO_4 in this industry provided a net savings of $8100/month above the operating expenses. Dialysis has also been studied in the recovery process.

In the film processing industry, tons of valuable metals go down the drain and recovery of silver alone could effect large savings. Some private laboratories, like those processing TV film, do recover silver but, in many cases, the quantities at any one location are very seldom large enough to warrant recovery measures. However, the General Services Administration and Bureau of Budget are looking into the feasibility of a recovery system for government generated waste silver solutions[34]. Table III summarizes by-product recovery in the plating and allied industries.

TABLE III

BY-PRODUCT RECOVERY IN PLATING AND ALLIED INDUSTRIES

Process	By-Product Recovery: By-Product	By-Product Recovery: Concentration Range (mg/l)	By-Product Recovery: Value ($/1000 gal.)	By-Product Recovery: Diminution of Pollutional Load
Rinse waters	Nickel	150-900	0.80-7.00	80-100%
	Copper	2-20 100-500	0.01-0.10 0.60-3.00	80-100% 80-100%
	Zinc	70-350	0.40-2.40	80-100%
	Silver	50-250	1.60-9.00	80-100%
	Chromium	400-2000	3.20-15.00	80-100%
	Cadmium	50-250	1.20-6.00	80-100%
	Brass	(Cu) 40-250 (Zn) 10-60	0.20-1.20 0.20-1.20	80-100% 80-100%
	Tin	100-600	0.80-4.80	80-100%
	Gold			
	Platinum			
Aluminum bright dip	Phosphoric acid	10%	$4,000	80-100%
Film processing	Silver			80-100%

MINING INDUSTRY

Acid mine water results from the exposure of sulfur and iron-bearing materials to processes of erosion and weathering. The drainage is generally acidic and contains sulfuric acid, ferrous, ferric, aluminum and manganese salts. In addition, the mine drainage may contain calcium, magnesium and sodium salts, carbon dioxide and silicic acid. The volumes of coal mine drainages encountered range from a few hundred thousand gallons/day to several tens of millions of gallons per day. An estimate of the magnitude of the problem in the United States[35] is that four million tons of sulfuric acid equivalent per year is being discharged to inland water courses. The regulatory agencies, in an attempt to control mine drainage, usually stipulate that the discharge should be alkaline with a pH range of 6.0 to 9.0 and a maximum iron content of 7 mg/l.

Recovery of sulfuric acid has been proved uneconomical and, therefore, there have been many processes reported for the treatment and disposal of acid mine drainage. These can be considered as three classes for convenience:

1. Lime neutralization process
2. Unorthodox or alternative processes
3. Limestone neutralization processes

The principle of these processes is that lime or other strong alkali is mixed with the acid mine drainage to neutralize the acids and to precipitate the contaminating metal salts which can be separated by sedimentation. However, the sludge formed has a high water content and presents a difficult disposal problem.

The acid mine drainage has been treated in many cases by lime to produce water for coal preparation plants and dust suppression purposes. The costs of treatment reported in one case was $1.09/1000 gallons, equivalent to a cost of 5.2¢/short ton of the coal produced[36]. As seen from this cost figure, lime neutralization processes are not economical, even though in some specific cases they may prove economical. Attempts to prepare marketable by-products such as rouge from acid mine drainage have been made without any success. Use of organometallic compounds for the production of pigments from acid mine drainage have also been reported[37]. The possibility of distillation and reverse osmosis processes have been discussed but the costs are prohibitive[38]. In summary, it can be said that none of the alternative processes has yet been shown to be cheaper than the lime process for general application, but it is possible that processes which lead to the recovery of potable water might be commercially viable in districts which are particularly short of water.

Limestone neutralization has found wide application in the neutralization of acid wastes other than those containing iron and other precipitable salts. Also, reagent inactivation is a problem when these salts are present. It may appear that the main advantage of using limestone would be the low cost of the reagent, but the fact of the matter lies in the separation and dewatering of the sludge of precipitated contaminants. Also, if an auxiliary process could be developed for the removal of ferrous salts, the use of limestone would be very effective. Biochemical oxidation of ferrous salts in acid solution appeared to be the only practical method and a new process using this technique was developed in England. Flow diagram of such a process is shown in Figure 13.

This new process has some limitations such as:

1. The concentration of dissolved iron and total acidity as calcium carbonate should be at least 10 and 25 mg/l, respectively.

2. The SO_4 concentration should not exceed 5000 mg/l.

3. The extreme temperature limits for the process are expected to be 0 to 35° C., with a preferred working range of 5 to 25° C.

4. Manganese salts cannot be removed.

However, it seems possible that over half of the acid coal mine drainages of the United States could be purified by this process. The cost of treatment employing biochemical oxidation and limestone neutralization is reported as 33¢/1000 gallons and for the lime process, it is 53¢/1000 gallons. For most contaminated acid mine drainages, the conventional lime process would be more applicable.

In an exceptional case, disposal of mine water from a mine of Bethlehem Mines Corporation, Pennsylvania[39], has been made profitable. Mine water was used as the cleaning medium for raw coal extracted from the mine. Raw coal had about 30% $CaCO_3$ and $MgCO_3$ and provided more than enough alkalinity to neutralize the acidic mine waste. The pH of the waste water was raised from 3 to 7 and iron content was reduced from 551 mg/l to 0.1 mg/l range. The quality of water was, thus, well within the local limitations and a possible financial liability of treating the acid mine discharge has been converted into an asset.

Leaching solutions from copper ore waste dumps[40] may be not only a profitable source of copper but also of uranium. The solutions pick up both metals as they percolate through piles of copper mine waste. A study by the U.S. Bureau of Mines' Metallurgy Research Center at

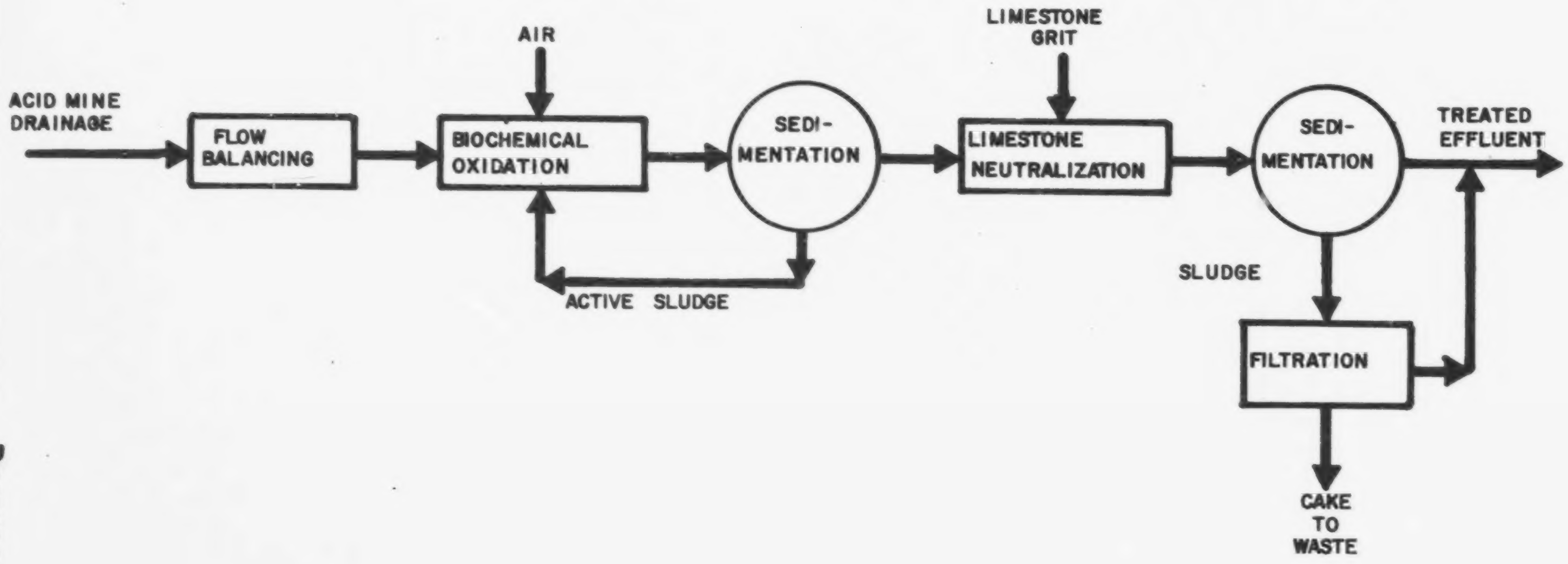
AIR
LIMESTONE GRIT
ACID MINE DRAINAGE
FLOW BALANCING
BIOCHEMICAL OXIDATION
SEDI-MENTATION
LIMESTONE NEUTRALIZATION
SEDI-MENTATION
TREATED EFFLUENT
ACTIVE SLUDGE
SLUDGE
FILTRATION
CAKE TO WASTE

FIGURE 13

FLOW DIAGRAM OF BIOCHEMICAL OXIDATION AND LIMESTONE NEUTRALIZATION PROCESS

Salt Lake City, Utah, has shown that economic recovery of both copper and uranium is feasible by ion exchange. The recovered uranium concentrates are pure enough to meet government specifications and are also suitable for nuclear power industry. It is estimated that an annual supply up to 1000 tons of uranium oxide could be assured by applying this process to all domestic copper leaching solution containing uranium compound.

Kennecott Copper Corporation[41] has developed a process for recovery of copper from mine tailings via precipitation process. The process is simple and works as follows: water that has percolated through the dump goes into a cone of precipitator filled with iron. In a reaction known as cementing, the iron goes into solution and copper precipitates. The red precipitate containing 80% copper is used as smelter feed and the water recirculated to the dump. This process has increased the production considerably (a factor of 2 to 3) because the yield from mine tailings dumps is nearly as much as the mine itself.

A hydrometallurgical process[42] has been used to recover nickel from sulfide ore concentrates. This process is essentially an ammonia-leach hydrogen reduction process and has the advantage of lessening air pollution problems because sulfur is not emitted, but rather is recovered as ammonium sulfate fertilizer. In the process, ammonia solution extracts Cu, Ni, and Co from mine concentrates containing Ni (10%), Cu (2%), Co (0.4%), Fe (30%) and S (30%). Nickel and cobalt are extracted from solution together by treatment with H_2S. Nickel and cobalt sulfide precipitates are filtered and processed separately for recovery. The remaining solution contains diammonium sulfate $(NH_4)_2SO_4$ and it is recovered by evaporation. The product processed is 40 tons/day Ni, and by-products recovered per day are 3000 pounds Co and 300 tons $(NH_4)_2SO_4$.

In the coal mines, coal fines of the -48 or -100 mesh fraction of the coal produced are being sent to settling ponds or sold at a low cost for reason of quality. Flotation process has been demonstrated[43] to increase the plant realization of fine coal successfully because of its low cost, easy adaptability and little supervision. Clear water can be reused in the plant.

Molybdenum oxide ores are generally discarded as plant wastes. A new process[44] developed applies acid leaching, charcoal adsorption, ammoniation and calcining to slime fractions of sulfide and oxide molybdenum ores. A production output of 1.5 pounds of molybdic oxide (MoO_3) was achieved for every ton of ore fed.

There is a program under way on the use of wastes from zinc mining and milling for steel-making industries at the University of Wisconsin sponsored by the U.S. Bureau of Mines[45]. The wastes are a possible source of burnt dolomitic lime (useful as a flux in steel making), iron oxide sinter for blast furnaces and elemental sulfur.

COAL BY-PRODUCTS

Coke and Gas Industry

Substantial by-product recovery is practiced in this industry and the by-products from gaseous coke-oven effluents include: ammonium sulfate, coal tars and oils, and coal gas[46,47,48].

Phenolic-containing liquors are a significant disposal problem since they impair the taste of the receiving waters, especially if chlorinated. Destructive dephenolization processes, biological and chemical oxidation were found to be unsuitable due to their high operating and capital costs, especially with the phenolic concentration. Recovery of phenol from the liquors solved the problem of pollution control in addition to providing credit because of the value of phenol. Solvent extraction (with benzene), activated carbon adsorption, steam stripping, and ion exchange have been employed to recover phenol from the liquors. In a tar distillation plant, Detroit, Michigan, Allied Chemical Corporation[47] recovered phenol from a waste stream containing 3000 to 10,000 mg/l phenolics and the effluent phenol concentration was brought down to less than 10 mg/l at solvent to waste ratio of 1 to 1 or less. The solvents used were readily produced at the distillation plant without any equipment changes and this resulted in economic and efficient waste water dephenolization. Also, caustic soda was used to regenerate the solvent rather than distillation.

Phenol[49] has been recovered by distillation by the Koppers process and the Heffner-Tiddy process, extraction with benzene and trichloroethylene and adsorption by activated carbon. Ammonium sulfate and ammonia are usually recovered by neutralization followed by crystallization of the salt and filtration.

It is important to note that a wide variety of cyclic and aromatic organics such as benzene, cresols, xylenes and naphthalenes are produced in coke ovens and are condensed from the gas stream. This production has formed the basis of the coal-based chemical industry for many years before the advent of the petrochemical-based industry of today.

Flue Gas Treatment

Sulfur and nitrogen oxides in gaseous effluents are a problem for the electric utility, sulfuric acid, fertilizer, metallurgical, and pulp industries. SO_2 is generally recovered by wet scrubbing while sulfuric plants catalytically oxidize any SO_2 in the effluent to SO_3 and recover H_2SO_4 by wet scrubbing. There are a number of processes that are used for recovery of sulfur oxides, as follows:

1. Simon-Carves-Cominco process, based on wet scrubbing with ammoniacal solution to produce ammonium sulfate and either sulfur or SO_2.

2. The soda ash - zinc oxide process, based on wet scrubbing with a soda ash solution that is regenerated with $Zn(NO_3)_2$ and lime with the production of SO_2.

3. The manganese oxide process, based on wet scrubbing with a manganese dioxide solution to produce SO_2.

4. Wet oxidation, based on the oxidation of SO_2 to SO_3 using ozone in a manganese sulfate solution. $MnSO_4$ is oxidized with air and ammonia to regenerate manganous dioxide and to form $(NH_4)_2SO_4$ for sale as a by-product.

5. The adsorption processes, based on the use of activated char in water (Pauling), multi-bed char adsorption (Reinluft), activated char pipeline contactor (Central Electricity Research Labs, Leatherhead, England, and USPHS), and alkalized alumina (U.S. Bureau of Mines and Central Electricity Research Labs).

Flue gas from power stations are used as heat source and nutrient supply for production of chlorella[50]. Chlorella, rich in protein and vitamins, is used to upgrade animal feeder. Electric utility industry[51], in burning 281 million tons of bituminous coal to generate about 65% of United States' total steam electric output, yields about 20 million tons of fly ash. About 10% of this fly ash is sold commercially leaving about 18 million tons of wastes to be dumped at costs ranging from 50¢ to $2/ton. Utilization of fly ash by the United States is poor compared to Western European countries. Fly ash could be used as a prime constituent and additive for construction materials. Fly ash makes concrete stronger and less vulnerable to freezing temperature. Fly ash can be used as a soil stabilizer and as a clarifying agent in waste water treatment plants and as a sludge conditioner.

In the Kraft pulping process, the burning of spent liquor is practiced to recover heat and chemicals. This practice releases dust and sulfur-bearing gases into the air. A venturi scrubbing system[52] removes 99% of the dust and the amount of H_2S released to the atmosphere is reduced to a great extent by an improved oxidation step.

In the power plants and industrial boilers, Cat-Ox process[53] is used to remove 100% fly ash and recover high strength sulfuric acid (H_2SO_4) for sale. The process flow sheet is shown in **Figure 14.**
Hot flue gas taken directly from the boiler at 950° F. is first passed through a dust removal system, a combination of mechanical separator and electrostatic precipitator. The gas then goes into a converter system (Figure 14) where about 90% of SO_2 is converted to SO_3. Flue gas from converter is cooled and high strength H_2SO_4 is obtained through the absorption tower. The residual H_2SO_4 mist contained in the flue gas from the absorption tower is removed in a mist eliminator and the flue gas free from dust and SO_2 is let into the atmosphere.

Table IV summarizes by-product recovery in coal by-products industry.

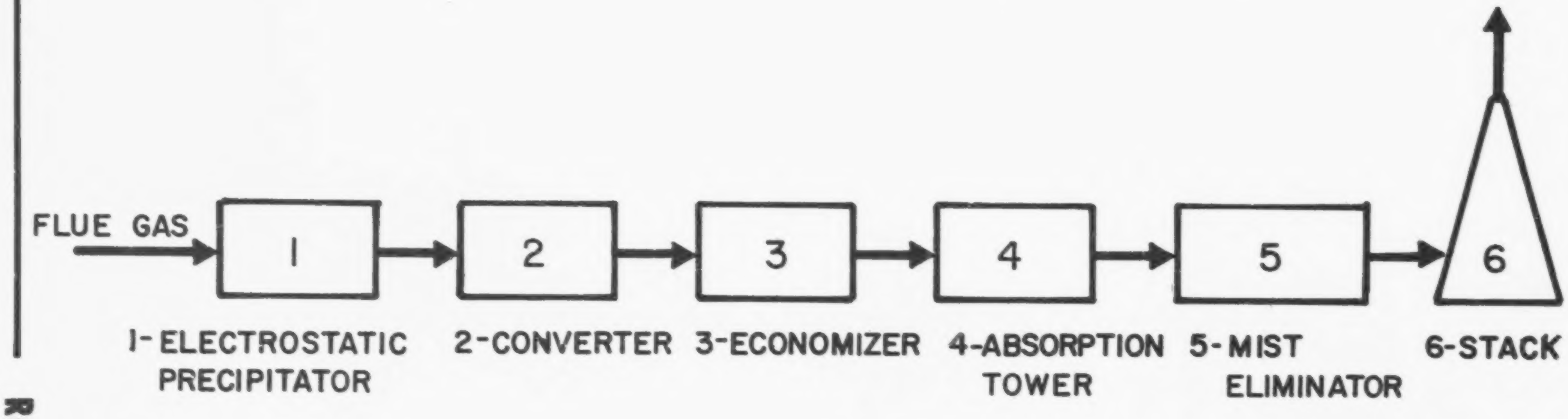
FLUE GAS
1
2
3
4
5
6
1- ELECTROSTATIC PRECIPITATOR
2-CONVERTER
3-ECONOMIZER
4-ABSORPTION TOWER
5- MIST ELIMINATOR
6-STACK

FIGURE 14

PROCESS FLOW SHEET OF FLUE GAS TREATMENT

TABLE IV

BY-PRODUCT RECOVERY IN COAL BY-PRODUCTS INDUSTRY

	By-Product Recovery			
Process	By-Product	Quantity	Value	Diminution of Pollutional Load
Coke plant ammonia liquor	Phenol	2 lbs/ton coke	$0.20/ton	40%
	Ammonium sulfate	24 lbs/ton coke	$1.00/ton	50%
	Ammonia	8 lbs/ton coke	$0.25/ton	50%
	Naphthalene Benzene Xylene Cresols	20 lbs/ton	$2.00/ton	100%
Flue gas scrubbing	Sulfur Sulfuric acid Ammonium sulfate	60 lbs/ton of coal burnt	$1.20/ton	80-100%

PETROLEUM INDUSTRIES

Petrochemical Industries

Petrochemical industries have been faced with the dealing of large amounts of organic wastes in their early stages of development. The reduction of pollutant load has been achieved by using organic wastes as fuel until recovery processes have been developed and a higher market for recovered chemicals developed. This approach has been followed in the production of almost every large volume petrochemical waste.

The more important recovery methods and products are presented below. Hydrogen is used in ammonia production, refinery operations, such as hydrotreating and hydrocracking, and many other purposes. Four recovery methods have so far been reported and the choice depends upon plant size, location, feed composition and hydrogen and use.

1. Wet scrubbing: is used to remove CO_2 and H_2 streams in conventional syntheses-gas plants. Scrubbing solutions include hot, carbonate-containing aqueous solutions, ethanolamines, and high pressure water.

2. Adsorption: is used on molecular sieves or activated carbon to separate hydrogen from hydrocarbons.

3. Cryogenic scrubbing: removes higher boiling impurities by condensation from low boiling hydrogen (-252.8° C.). This process is useful where a refrigerant, such as liquid air or nitrogen is readily available, as in partial oxidation synthesis gas plants.

4. Membrane permeation: is based on palladium's selectivity in passing hydrogen and is used to recover hydrogen from petroleum effluents.

Other petrochemical recovery processes:

1. Distillation: is used to recover chlorinated hydrocarbons following the chlorination of methane, olefins from the thermal production of ethylene, acetaldehyde following the production of vinyl acetate, and solvents from rubber latexes.

2. Crystallization: is used to separate xylene from ethyl benzene.

3. Adsorption: is useful for the recovery of carbon disulfide, carbon tetrachloride and other solvents.

4. Extraction: is useful for the recovery of isobutylene, naphthalenes, paraffins and phenol from a variety of wastes, and organic dyes are extracted following adsorption on fuller's earth.

5. Ion exchange: recovers basic amino acids, amines, alkaloids and organic acids.

6. Oxidation: regenerates spent caustic.

Petroleum Refineries

The recent trend in the newly constructed petroleum refineries is full integration of in-plant procedures and multi-stage waste water treatment combined with reuse and reclamation of purified water, resulting in considerable progress in pollution abatement and a drastic reduction of clean water intake requirements.

Use of hydrogenation processes, such as hydrosulfurization, yields products low in sulfur and, therefore, require minimum subsequent treatment. Application of chemical treatment processes, especially for gas scrubbing, allow complete regeneration and recovery of the solvent. The amount of spent chemicals requiring treatment and disposal is brought down to a low level by these processes.

Separate collection of waste water is employed in sewer systems according to their subsequent treatment. Efficient pretreatment such as evaporation, stripping of sour water condensates and equalization of flow and strength of waste waters are some of the processes used to improve product recovery and reduce waste load. Treated waste water is used as make-up water for recirculation cooling systems. In consequence of these measures, specific water consumption and waste water discharge per production unit has been in the remarkably low range of 9 to 22 gallons/barrel oil processed and 3 to 8 gallons/barrel of oil processed, respectively[54].

There are many by-products that could be recovered from petroleum refining wastes, even though all of them may not bring economic benefit. Therefore, the concept of by-product recovery is limited to those materials which, if recovered, would accrue some economic benefit, but not necessarily enough to cover the cost of recovery.

Based on this definition, the major by-product is sulfur, which is recovered from sour waters and from the hydro-treating process. The value realized through sulfur recovery is expected to increase greatly in the near future, due to the increased demand for low-sulfur fuels brought on by more stringent urban air pollution controls.

A number of refining process wastes have been recovered or reused and they are as follows:

1. Recovery of H_2SO_4 from sludges produced in the acid treatment of oils. Hydrolysis of the sludge produces a dilute (30-60%) black acid of rather limited utility.

2. Reuse of spent alkylation acid in the treatment of oils and waxes, with subsequent regeneration in captive or outside acid plants.

3. Sale of high-phenol waste caustics from treatment of catalytically cracked naphthas.

4. Use of sprung phenols as refinery fuels. These materials come from acid springing of spent caustics from cracked naphtha treatment.

5. Use of various waste acids in slop oil treatment.

6. Recovery of aluminum chloride from hydrocarbon sludges.

7. Recovery of acid oils by reaction of waste caustics with acids.

8. Use of boiler feed water treatment sludge in the neutralization of waste water.

9. Reuse of treated waste water to supplement normal refinery water supply.

10. Recovery of ammonia and hydrogen sulfide from sour water stripping for use as raw materials in the manufacture of fertilizer grade ammonium sulfate.

Production of single cell proteins from petroleum has been shown feasible and the proteins can be used as animal or human feed supplements[55]. The price of a 50% protein single cell is estimated at 6 to 8¢/pound and hoped to be competitive as a potential animal feed supplement. For human consumption, the protein could command a price in the range of 30 to 40¢/pound. But it is feared that the cost of production of proteins is likely to mount up because of the uncertainties involved in additional processing. Another big hurdle will be probably in marketing or acceptance of such products due to factors like flavor, color, appearance, personal and cultural idiosyncrasies of consumers.

A $5.6 million plant is going into action in 1970 for the commercial production[56] of protein from petroleum. The concept consists basically of letting microorganisms grow big in bulk by nourishing themselves on hydrocarbons; the bulked product can be processed for foodstuff use. About 100 tons of gas oil will be needed to produce 100 tons of protein.

A single stage extraction vessel is used as a petroleum refiner's latest weapon for taking obnoxious phenols out of water from catalytic cracker distillate drums before it is let into the sewer. The extractant is light catalytic cracker cycle oil which is subsequently processed to finished heating oil. Using this principle, Humble Oil Company in Baton Rouge, Louisiana, is accomplishing a 75% reduction in phenol.

Aluminum chloride waste results from the petroleum and petrochemical industries, due to the use of aluminum chloride as a catalyst, and this cannot be discharged to stream or municipal sewer system, due to its low pH and high dissolved solids. Spent aluminum chloride is available in the form of about 27% aluminum chloride (32° Be') solution. The handling and disposal of such inorganic salts are troublesome and are not in the realm of current economic feasibility. However, such troublesome products can be used to control or eliminate other environmental problems. One such case[57] is the use of waste aluminum chloride solution in the field of waste water treatment for effective solids separation, phosphate removal and sludge conditioning. The present estimate is that some one hundred to two hundred million pounds/year will be available as 32° Be'solution and that more than 90% of it is recoverable. At the current cost of 32¢/pound of aluminum, the cost of 27% aluminum chloride solution is estimated at 4.4¢/pound and the total value of the waste aluminum chloride amounts to 6.6 million dollars.

Recovery of Oil From Waste Waters

Spills of oil constitute a major pollution threat to the water resources of the nation. Both water and land-based facilities are sources of this danger to our streams and rivers. Much damage has already been done from accidental or indiscriminate spillage of crude oil, petroleum and its by-products. Such spills have contaminated water supplies, killed fish and wild life, created fire hazards, and destroyed or reduced the usage of recreational areas.

The major sources of oil pollution include: gasoline service stations, oily waste industries, offshore oil and gas operations, oil tankers and industrial transfer and storage of oils. Cleaning up an oil-contaminated area is time consuming, difficult and costly. In addition, the losses due to destruction of fish and other wild life, damage to property, contamination of public water supplies and any number of other material and aesthetic losses are involved. These losses may be very great and extend for months or years, sometimes for decades, depending on the quantities and kinds of oil involved.

It is estimated that about 350 million gallons of used motor oil must be disposed of annually by the more than 210,000 gasoline filling stations. These stations are the key suppliers of used oil re-refiners. Re-refined oils are used in railroad journals, to freeze-proof coal, as dust control for rural roads and as motor oils and industrial lubricants. In the recent years, more than half of the re-refiners have gone out of business due to changes in labeling requirements and in the tax laws. Also re-refining has now become a marginal business. As the demand for used oil for re-refining diminishes, more of the waste oil will be disposed in other ways leading to pollution of natural water courses. Therefore, it is imperative, at this stage, that proper measures should be developed to provide incentives to collect and reuse these oils rather than disposing of them. The disposal of waste mineral oils and greases, such as those from garage and filling stations, to sewer systems are being prohibited by ordinance due to the treatment problems and their flammability and potential explosive hazard.

There are about 10,000 industrial plants in this country having significant quantities of oil in their wastes. Technology is now available to cope with wastes having either floating or emulsified oil. The more or less standard procedure of removing floating oil is with API separator. The performance of API separator is limited to the separation of solids and immiscible liquids which are susceptible to gravity separation. Stable emulsions and substances in solution cannot be separated by gravity differential principle. The use of H_2SO_4 for pH control and aluminum sulfate for floc formation is practiced for removal of soluble oil in metal-working plants. The skimmed oil is sold to an outside concern who reclaims it for various commercial uses. For emulsions, strong acid or salt may be used to de-emulsify and then the oil is separated by conventional method. Dissolved air flotation has also been used for removing the oil and improving the quality of the separator effluent with the reduction of oil and free solids content.

The Oil Pollution Act of 1924 and subsequent ammendment in 1966 require that willful or grossly negligent dischargers of oil from a vessel remove the oil from the navigable waters and adjoining shorelines immediately. To minimize pollution, such as the Torrey Canyon disaster, clean-up measures must be taken promptly and these are expensive. When the responsible parties cannot be identified immediately, or fail to act expeditiously, the initiation of effective clean up and recovery of clean-up cost poses a problem due to the present fiscal and legal difficulties. Some of the leading oil-spill treatments are listed ~~in~~ the accompanying pages.

A new process developed by Edgar Clarke[58], under a FWPCA grant, is said to recover high quality, fine particle carbon black (valued at

8 to 12¢/pound) that used to be a waste product. The process involves the following steps:

1. dehydrate, neutralize oil with caustic soda,
2. dilute with light naphtha and remove solids,
3. distill, and recycle naphtha,
4. vacuum distill off products,
5. heat with activated clay; use spent clay for land fill.

Berks Associates (Douglassville, Pennsylvania) using Clarke's process, report that their products obtained by re-refining used lube oil are fully comparable to those produced by major oil companies and the cost of producing them is less than the 20 to 22¢/gallon reported by the majors. There are recovery units in operation ranging in size from 20,000 to 100,000 gallons of lube oil per day. Schofield and deVries (Toronto) is marketing a process for recovering heating oils, and Comprino N.V. (Copenhagen) is planning to build 100,000 gallon/day units across Europe. A 150,000 gallon/day unit is under planning for the reprocessing of industrial wastes such as cutting oils, soluble oils and certain rendering-house fats and oils. The end products from this new unit will be non-lubricating oils with a variety of industrial applications.

Engine plants of the Ford Motor Company at Cleveland[59] recover and reuse oil from waste water. The disposal, efficient recovery and secondary utilization of waste products presented a unique and difficult challenge to the plants. The output of the 0.8 million gallon/day waste treatment plants consists of clarified water, a sludge slurry and skim oil. The sludge slurry from the clarifier is transferred to holding lagoons for disposal. Soluble oil is manufactured from the reclaimed oil following the process shown in the accompanying flow diagram (Figure 15).

The performance of the reconstituted soluble oil demonstrated it cannot only match the performance of the proprietary soluble oils but also excel in some qualities such as rust protection, non-formation of "leopard spots", cleanliness and odorlessness. Thus, the recovery and reuse of what was once considered a practically worthless waste product was shown productive and can bring significant cash savings.

SOME LEADING OIL-SPILL TREATMENTS

Developer	Product Name(s), Composition Action & Treatment Level	Unit Cost & Estimated Cost/Gal. of Oil Treatment	Where Used
Alken-Murray Corp. New York, N. Y.	Alken OSD Dispersant, non-ionic/anionic detergent mix, in solvent carrier, emulsifies oil. Treatment level: 7 to 10% by volume (higher for heavy oil in cold seas).	$3.00/gal. (25¢)	Offshore drilling rigs; jet fuel spills; loading docks & paper mill spills.
American Machine & Foundry Co. Stamford, Conn.	Underwater injection of air repels oil, debris & trash.	---	A Connecticut beach.
American Oil Co. New York, N.Y.	Oil, absorbed in boat-mounted polyethane foam, is squeezed out.	---	Tests on inland waters.
Cabot Corp. Boston, Mass.	Cab-O-Sil, silane-treated silica (collodial) acts as a wick in thicker oil spills. Treatment level: 1 to 4% by weight.	$2.00/lb. (25¢)	Tests on inland & sea waters.
Cyprus Mines Corp. United Sierra Div. Trenton, N. J.	Mistron Vapor, micronic talc powder for beach clean up via agglomeration. Mistron ZSC, zinc stearate coated grade designed for the open sea.	$3.50 for a 50 lb. bag.	Ocean Eagle spill.
Drew Chemical Corp. Marine Div. New York, N. Y.	Ameroid Oil Spill Emulsifier #1, wetting and emulsifying agents in an oil-soluble liquid.vehicle. Treatment level: 3 to 5% by volume.	$2.77-3.25/gal. (10¢)	Torrey Canyon, General Colocotronis Ocean Eagle

SOME LEADING OIL-SPILL TREATMENTS (Continued)

Developer	Product Name(s) Composition Action & Treatment Level	Unit Cost & Estimated Cost/Gal. of Oil Treatment	Where Used
Economics Laboratory Magnus Marine Div. New York, N.Y.	Mix of non-ionic solubilizers and dispersants in a penetrating carrier. Treatment level: As low as 1/2% by volume.	$2.00-2.58/ gal. (5¢)	General Colocotronis
Enjay Chemical Corp. Linden, N.J.	Corexit 7664, mix of proprietary & purchased food-grade emulsifiers. Treatment level: As low as 1 to 2% by volume.	$3.50-4.00/ gal. (10¢)	General Colocotronis, Esso Essen (Capetown, South Africa)
Guardian Chemical Corp. Long Island, N.Y.	Pyrexon, liquid & powder, mixed with oil, promotes burning by wicking and catalytic oil breakdown. Polycomplex A-11, used to disperse unburned oil. Treatment level: 13 to 25% by volume.	$2.90/lb (10¢)	Laboratory & field tests.
Midland Silicones Ltd. (subsidiary of Albright & Wilson) Aberthaw, Wales	Silicone-treated flyash is dusted on the spill, sinking it. Material biochemically degrades on sea bottom. Treatment level: 250% by weight.	$24-36/ton (40¢)	Lagoon near Aberthaw generating station.

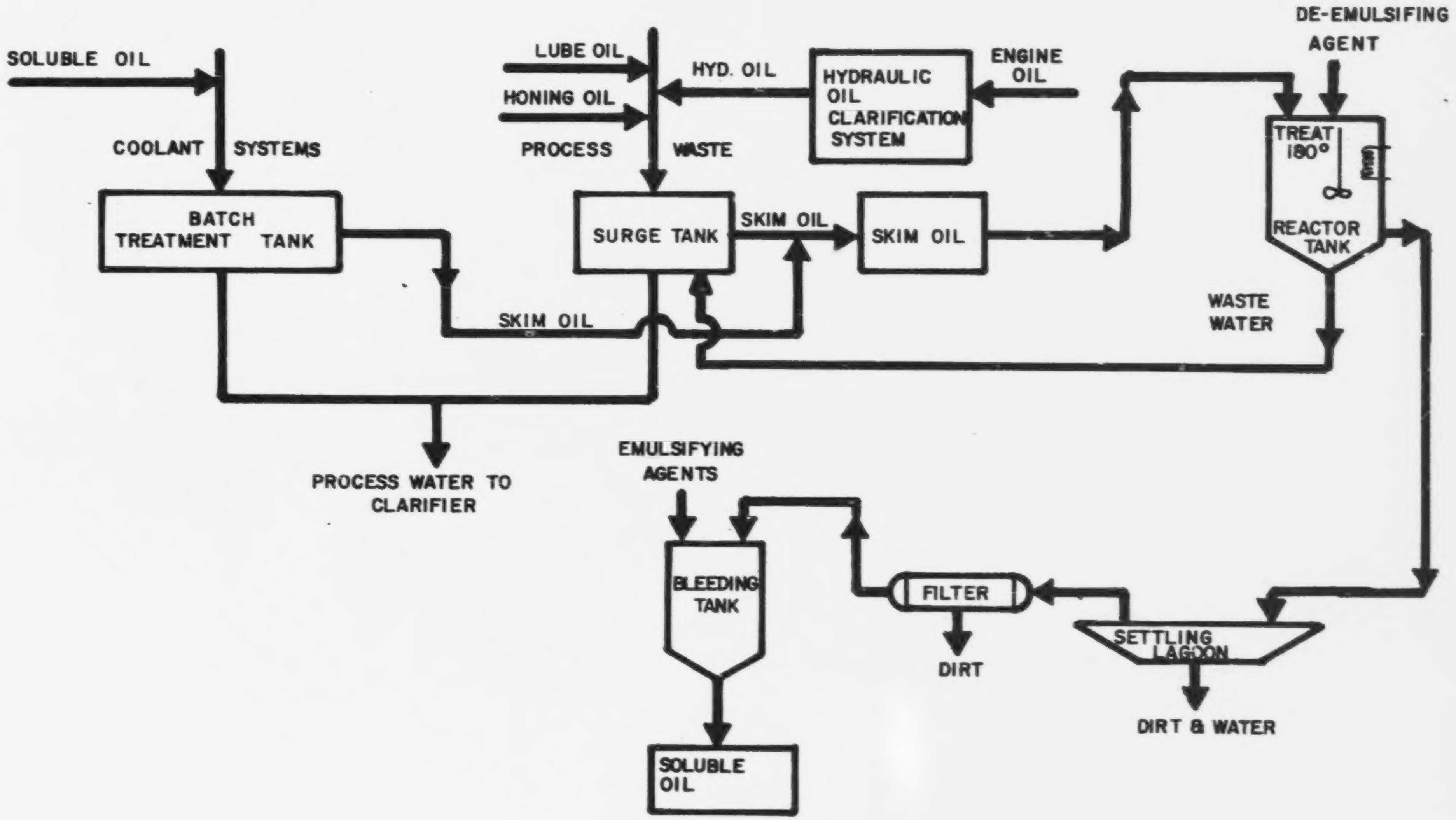
SOLUBLE OIL
COOLANT SYSTEMS
BATCH TREATMENT TANK
LUBE OIL
HONING OIL
PROCESS WASTE
HYD. OIL
HYDRAULIC OIL CLARIFICATION SYSTEM
ENGINE OIL
DE-EMULSIFING AGENT
TREAT 180°
REACTOR TANK
SURGE TANK
SKIM OIL
SKIM OIL
SKIM OIL
WASTE WATER
PROCESS WATER TO CLARIFIER
EMULSIFYING AGENTS
BLEEDING TANK
SOLUBLE OIL
FILTER
DIRT
SETTLING LAGOON
DIRT & WATER

FIGURE 15

RECOVERY OF SOLUBLE OIL FROM RECLAIMED OIL

SLUDGE DISPOSAL AND BY-PRODUCT RECOVERY

Sludge handling and disposal have often been the most troublesome aspect of water and waste water treatment. Disposal of dried sludge as a fertilizer or soil conditioner has been practiced for many years. Preservation of organic matter in this fashion has a great appeal to conservationists, but the trend is to alternate methods of disposal because of economics. Usually, the value of sludge as a fertilizer is limited because the nitrogen, phosphoric acid and potash content is too low. The organic material in sewage sludge does, however, make it a desirable soil conditioner.

Even though using sludges rather than disposing of them is an applaudable concept, waste sludge utilization need not necessarily be profitable, but it could be a means of reducing sludge disposal costs. Among other factors, market value of by-product and marketing problems that may be encountered are of prime importance while evaluating by-product recovery. The market place determines the by-product specifications and the specifications are rigid involving product purity and concentrations. The waste sludge processing cost to meet rigid specifications are very high and, therefore, industries who have attempted product recovery concluded that it is much easier to sell or give the material to a refiner who assumes responsibility for its ultimate disposition.

The recovery of vitamin B-12 from sewage sludge has been frequently discussed in the literature because of its value as a supplement to animal feeds. Vitamin B-12 has been successfully recovered from dried, undigested activated sludge in pilot plant studies. Extensive studies[60] at Milwaukee determined that B-12 is derived, in part, from raw sewage and partly from biological synthesis in the activated sludge aeration tanks. The B-12 production process at Milwaukee started with the dried waste activated sludge (Mil organite) and concentrated liquor was extracted following multiple-effect washing[61]. The liquor was further concentrated to produce B-12. The pilot plant operation indicated 308 pounds of pure vitamin B-12 could be produced each year from 70,000 tons per year sludge supply.

The Metropolitan Sanitary District of Greater Chicago, in cooperation with the University of Illinois, studied the value of heat dried activated sludge as an additive to animal feed[62,63]. After feeding with chicks, pigs, etc., it was concluded that sludge was a successful beneficial additive if limited to a small percentage of the total animal feed.

When sewage has a very high grease content and low alkalinity, a process known as "Miles Acid Process" was found to be very effective for extracting grease from raw sewage solids[64].

In the case of oil-bearing waste waters containing a complex mixture of lubricating oils, cutting oils, and emulsion coolants which are either soaps or synthetic detergents, lagooning is the accepted practice prior to final disposal of the sludge. However, by the use of ferric chloride and lime, sludge can be settled out as ferric hydroxide. Recovery of iron coagulant has been shown to be both feasible and economical[65]. The recovery is accomplished by redissolving the iron hydroxide sludge with 66° Be' sulfuric acid and liberating the absorbed oil. The recovered iron coagulant is in its sulfate form and reused in treating the waste.

It should be noted here that the cost of disposal is eliminated by this method in addition to coagulant recovery. On the basis of a million gallons of waste water, a net reduction in cost of $274 was achieved by the recovery method as compared to the conventional method.

Within recent years, much interest has been directed to removal of phosphate from treated sewage because of the unsitely and nuisance growth of algae attributed to the phosphate content of sewage effluent. Alum has been found to be an effective coagulant and is in much use by sewage treatment plants. It is anticipated that research will be directed to recovery processes of aluminum from the hydrous sludge with phosphate remaining in the residual sludge. By-product recovery is greatly desired in this case because of the serious problem of disposing of the alum-floc sludge.

The disposal of sludges resulting from the clarification and softening of raw water at water treatment plants has not been as much of a problem as waste water sludge disposal, but it is becoming more critical every day. Disposal by dilution into surface waters is simple, inexpensive and acceptable to many state regulatory agencies without prior treatment. It does not have much effect on the dissolved oxygen content of the receiving waters but it can be a nuisance because it produces turbidity and forms sludge banks.

The water plant sludge has been added to the municipal sewerage system in many cases. It is believed that the sludge functioned as a raw sewage flocculent and, thereby, improved the overall sewage treatment efficiency[66]. However, if the dumping of water plant sludge is not proportioned over a period of time, it may inhibit biological treatment processes.

One discernible trend in water plant sludge handling has been the increased use of recovery techniques. Water works sludge recovery is generally considered as an alternative solution to disposal only where lagooning and dilution were not feasible and hauling to distant farm land was not economical.

The sludges removed from sedimentation basins consist of a dilute suspension of aluminum hydroxide among other things such as algae and silt. Reclaiming alum from the hydrous sludge and reusing it for raw water flocculation has been shown feasible. Investigations in England determined that sulfuric acid could be used to convert insoluble aluminum hydroxide to aluminum sulfate which could be reused as a flocculent[67]. With the decrease in pH, the alum recovery was found to increase and at a pH of 3, the recovery was 60 to 65%.

At Tampa, Florida[68,69], it was estimated that 1180 pounds of 93% sulfuric acid were needed to produce 2000 pounds of reclaimed alum (17% Al_2O_3) at a 90% yield. Cost of commercial alum at $38.08 per ton and sulfuric acid at $19.48/ton, it was estimated that about $26/ton could be saved by using reclaimed alum. The above cost figures must be modified and interpreted in relation to the overall water treatment costs; the recovered flocculent is most likely to have a lower efficiency than the original commercial alum and require higher dosages. As recovery is not complete, some commercial alum must be added.

Recovery of softening-plant sludges can reduce the overall plant operating costs, but it involves numerous operational problems. First, magnesium has to be excluded from the sludge and this is achieved in the centrifuges often at the expense of solids capture efficiency. Second, split treatment procedures can be adopted, but neither calcium carbonate nor magnesium hydroxide flocs settle separately. Third, dewatering and calcining equipment requires substantial maintenance and moderate operating budgets. Fourth, sludge reclamation often does not eliminate the need for alternate sludge disposal facilities because not all of the sludge is processed. A final disadvantage results from changing water quality with the seasons. Variable sludge quality complicates calcining operations.

More and more water treatment plants are adopting lime and alum reclamation processes and the cost of water treatment has been reduced by varying degrees wherever reclamation has been in operation. For further reduction in cost of operation, improvement in efficiency, additional research is needed in this field. When the reclamation process becomes more economical than what it is now, all the new plants would be designed with reclamation facilities.

HEAT RECOVERY OR UTILIZATION

Environmental changes due to thermal pollution such as stratified flow, the effects of temperature on the biota, and the effects of temperature on the physical and chemical properties of our receiving water are becoming quite critical[70]. The three major sources of thermal pollution are as follows:

1. Steam-generating industries.

2. Steam and/or power-generating industries.

3. Process streams from wet process industries.

When the temperature of the waste is very high, heat recovery is very attractive and practical. When the temperature difference is relatively small, heat recovery is not practical due to poor economics. However, there are a number of companies that have made equipment available for the recovery of heat from low temperature differential wastes. Therefore, recovery of heat and utilization for more efficient power generation is feasible and should be practiced wherever possible in order to eliminate thermal pollution. Numerous cases of heat recovery to produce process steam is practiced in the organic and inorganic chemical industry.

The other feasible method of controlling thermal pollution is water quality management[71]. This involves flow regulation, discharge outfall design and heat storage with controlled releases. Though this method does not bring in direct benefits, the cost involved in water quality management works would be much less than the construction of conventional cooling towers, ponds and so on.

The method that offers the greatest promise for thermal pollution control besides heat recovery is the utilization of waste heat in agriculture, aquiculture or for miscellaneous industrial applications. There are a number of FWPCA studies under way on this aspect[72].

The present trend in the thermal pollution control seems to be that the cooling towers and ponds must be used only where no other solution is available, and efforts to devise other more productive methods of heat control and recovery will be undertaken in the future.

MISCELLANEOUS INDUSTRIES

Breweries and Distilleries

In the brewing industry, settled yeast from a previous fermentation is used in the fermenting of beer to initiate fermentation in the next batch. There is always an excess of yeast above the requirements of the brewery and only part of this yeast is satisfactory for further use in the brewery as the yeast, while settling, carries down some materials that are not desirable in beer. The undesirable part of yeast is generally discharged to the sewer. Though it is not harmful to plant operation, it has a very high BOD and becomes objectionable. This product could, however, be dried and used for cattle feed.

Distilleries discharge their wastes from molasses fermentation to the sewers or receiving waters. When this waste is evaporated and dried, it was found to be an excellent source of vitamin B complex and showed a substantial profit above the cost of evaporation and drying for use in producing cattle feeds.

Wastes from brewery and distillery fermentation have been converted to valuable by-products for many years. The two major by-products are high-priced animal feed and brewer's yeast. Spent grain mash used to be a serious water pollution problem, but the distilling industries have recovered more than 90% of their fermentation residues for sale as animal feed[73]. The residue has a high concentration of vitamins and protein that, when mixed with other materials, makes a premium cattle feed.

Residual yeast from brewery and distillery fermentation is also valuable as an animal feed because it contains vitamin B complex, protein and essential minerals. Drying stabilizes the residual yeast by deactivating the enzymes in addition to improving the yeast's digestability. However, it is believed that a brewery must have at least about one million pounds of yeast solids per year to justify drying equipment.

The process of manufacturing tartaric acid and tartarate salts from winery wastes during World War II is considered uneconomical now[74]. The pomace portion of the waste has been used as a vineyard soil conditioner or sometimes dehydrated and sold as a cattle feed supplement and plant mulch.

Food Industries

The food-processing industries have been faced with the realization that both water supply and waste disposal are limiting factors in growth, operation, and product cost. Water-saving techniques have, in many cases, permitted increases in plant capacity without additional burden on fixed resources. In some cases, these have brought significant savings in total production expense.

Where water conservation is practiced, there are concomitant changes in waste quantity and character. With increased production, the total organic waste load has inexorably risen and the problems attendant to disposal have become increasingly difficult to solve. Process advances have produced some new waste constituents and water economics have resulted in concentration of waste loads in certain process streams.

Faced with a general expansion in the potential waste load which must be treated or transferred to receiving waters, regulatory authorities have been forced to tighten controls and stimulate industry's critical examination of its contribution to the pollution problem. Municipalities which receive the wastes of their allied industries assume responsibility for augmenting treatment capacity and impose the industries with service charges to transfer costs of expanded facilities and operation.

The seasonal character of wastes from the food-processing industries and their relatively high proportion might suggest that it might be more economical to treat the separate components rather than the combined flows. Industries, in seeking ways to reduce costs, are becoming increasingly aware of their responsibilities in pollution control and have begun to explore the economic feasibility of "in-plant" modifications to reduce waste and of "on-site" facilities to provide treatment.

The state of the art in food processing plants appears to involve continuous recirculation of waters with limited make-up and blow-down for a particular subprocess. For example, in the canning industry, wash waters for most produce can be continuously recycled within an optimum system. Final rinsing removes the residual dirty water and this serves as make-up for the initial scrub washing subprocesses. Similarly, flume water used for the carriage of fruits and vegetables is continuously recycled and builds up a high organic content. Low pH and appropriate bactericides can be used as a means to control bacterial growth.

Cooling tower recirculation is a common method of conserving water. The cooling tower blow-down can be used for supply water with the various subprocesses of the packing plant. Evaporator waters may be reused for processes, especially initial washing, etc. The increasing costs of water and sewer service charges based on flow volume and pollution content, are acting as incentives to optimize the conservation and reuse of water within the food-processing industry. Recent surveys of eleven California canneries[75] indicate that water conservation and reuse can reduce water use per unit of product up to 40%. The sludge from the food industries is a major concern to the industries because of high moisture and fibre content plus a lack of stability which complicates storage of the seasonal production. However, the industries have shown keen interest in using waste products to increase profits and reduce air and water pollution.

The use of waste activated sludge from the citrus industry has been evaluated as a source of vitamin B and protein. Vitamins of the B group contained in this sludge include: thiamin, B-12, riboflavin and niacin[76]. After the sludge is filtered, dried and pulverized, it is used as an animal feed supplement.

Citrus pulp has been extensively used by itself as a cattle feed. After dehydration, the pulp has been sold for $30 to $45 per ton[77,78]. Without dehydration, citrus wastes have been sold as cattle feed for $4 per ton or converted to molasses and sold for $45 per ton. Pectin is also made from citrus wastes and used in jams and jellies.

The disposal of wet solids from the canning industry has been a major problem. Composting has been investigated and seems promising. A portion of the total canning waste has been dehydrated and used for animal feed[79]. The total cost of producing this feed was reported to be $47 to $53 per ton of feed. Even though there is a net cost to the industry, the by-product utilization is cheaper than other methods of disposal.

The potato processing pulp is used as a cattle feed[80]. Dewatering and drying of pulp is difficult because the solids are hydrophilic. In large plants, the 5 to 13% solids pulp is dewatered to 30 to 35% solids by pressure filtration after conditioning the pulp with lime. In an attempt to keep the peels away from water-borne wastes, dry-caustic peeling process[81] is used. In this process, potatoes are sprayed for 50 to 100 seconds with 20% lye solution at 170° F. and drained. Then potatoes are subjected to infrared heat for 2 to 5 minutes following the holding at room temperature for 5 minutes. The peels are removed in the rotating rolls and during tumbling. The discarded peels are sold as cattle feed.

Pressure on food and pulp process has generated a parade of recent processes to upgrade liquid and solid wastes. The impetus behind this flurry of activity is the need to find dollar incentives for pollution prevention. Leading among the new processes are those that use yeast, bacteria and even laser beams to convert pollutant beans into edible products. Swedish Sugar Company[82] has announced a process that will treat a potato-starch filled waste stream with a symbiotic combination of endomicopsis and candida yeasts. The end product suitable as animal feed is 50% protein, a mix of 95% candida yeast and 5% endomicopsis.

The wastes produced in this industry are largely organic and of a highly biodegradable nature. Therefore, product recovery is very much limited. However, solid wastes, in a few instances, have been utilized in many ways. Tomatoes have been pressed and dehydrated for use as hog or cattle feed. Pea vines, corn husks and corn cobs have also had limited sales. Citrus peel wastes may be pressed for molasses which can be processed, dried and sold as cattle feed. Installation of flash evaporators to produce the molasses has significantly reduced the waste load discharged. Also, certain types of pits and nut shells have been converted to charcoal.

Due to the low value of these by-products, the primary benefit to the food industries at this time is the avoidance of the cost of hauling wastes to a landfill. With the increase in cost for solid waste disposal, it is anticipated that new by-products will be developed. It should be noted here that there is a definite indication that many of the small firms are hard pressed to compete and the percentage of small firms will decrease in the future, as a result. The principal difference between old, prevalent and newer technology in these industries is not in the operational sequence, but rather in the speed and efficiency of the machinery performing the operations. New production machinery is expensive and can be justified by adequate production volume only.

Fertilizer Industry

The phosphoric fertilizer industry is faced with a difficult task of improving its gaseous effluents. Fluoride-containing gases are produced from the reactors and evaporators and collected by using spray boxes, wet impingement, wet-centrifugal spray and wet-impingement tray scrubbers. The fluoride content of these liquors, present as hydrofluosilicic acid (H_2SiF_6), represents a problem and an opportunity. The fluoride evolved during wet acid, phosphoric acid, superphosphate and triple superphosphate production in the United States is equivalent to the total United States production of hydrofluoric acid. Hydrogen fluoride is the source of fluorine compounds used in the production of aluminum, fluorocarbons and other chemicals. The availability of high grade fluorspar ore, the main source of hydrofluoric acid, is limited and these liquors represent an increasingly important source of fluorine. The hydrofluoric acid, 25% in concentration, can be used as fluorinating agent for public water supplies and may be converted into sodium silicofluoride for both this purpose and for ceramics and glass manufacture. Hydrofluosilicic acid has been suggested as a fluorinating agent and the use of strong dehydrating and decomposing agents for producing hydrofluoric acid from fluosilicic acid has also been studied.

In the recent years, attention has centered on conversion of hydrogen fluoride synthetic cryolite (Na_3AlF_6) or aluminum fluoride (AlF_3)

for use in Hall cells. There are two commercial routes of conversion:

1. The acid is contacted with an alkali such as ammonia to produce the alkali fluoride and a filterable powdered silica that can be marketed for use as a thickening agent, for rubber and plastic additives and for other purposes. The alkali fluoride is reacted with an aluminum salt to produce the alkali cryolite which may be converted to sodium cryolite by fusion with a sodium salt[83].

2. The acid is reacted with aluminum hydroxide $[Al(OH)_3]$ to produce aluminum fluoride (AlF_3) and silica (SiO_2)[84].

In the ammonium phosphate plant, the exhaust air stream from ammoniator contains high ammonia and, therefore, it is recovered by using acid stream scrubbers from both economical and a pollution control point of view. The initial cost and operating expenses for such installations are very high and the returns from the recovery of ammonia are just enough to compensate for operating cost. Therefore, fertilizer industries are generally reluctant to install such systems that cover only operating expenses. However, industries do expend large capital outlays in order to reduce complaints and improve public relations.

Most of the fluoride wastes effluents from the fertilizer industry are aqueous type and some are airborne. The airborne fluoride compounds become waterborne when they have been scrubbed with water or with aqueous alkaline reagents.

When product recovery is not practiced, due to the small quantity of waste or too low a concentration for recovery, the waste is treated and discharged to receiving water course or sewer. The treatment facilities essentially involve the following steps:

1. neutralization of waste water with hydrated lime at a pH value slightly above 11, which results in the formation of relatively insoluble calcium fluoride,

2. separation of the insoluble product of the reaction in a continuous clarifier,

3. vacuum filtration of the sludge, and

4. acidification of the clarifier effluent to lower the pH value to within the range of seven to nine.

Clarified effluents contain less than 20 mg/l of fluoride ion and by allowing it to stand for several hours, post precipitation of fluoride salt occurs resulting in the further decrease in the fluoride concentration. Where required, additional fluoride removal may be obtained by passage of the fluoride waste through a bed of activated alumina regenerated with sulfuric acid or through bone char regenerated with sodium hydroxide.

The other important by-product from sulfuric acid-based phosphoric acid plants is gypsum ($CaSO_4$) which has been used in wallboard and cement and for the production of sulfur via reduction with coal, followed by fixing of the lime--either with silica or by reaction with ammonia[85]. Such practices are in use in sulfur-short locations and may become less attractive as the sulfur supply situation improves.

Gypsum, derived from the production of wet process phosphoric acid poses major problems because it does not have a good market. Storing of gypsum is practiced in some cases and this is becoming expensive because of the increasing land value.

At 1969 production level, on an average of 5 tons gypsum/ton of 100% phosphorus pentoxide, about 20 million tons of gypsum are produced per year. There are seven major plants throughout the world which practice recovery of sulfuric acid and cement. Following this process, it is forecasted[86] that 1500 to 2000 tons of sulfuric acid per day and about the same amount of cement can be recovered and there will be a $25 to $30 million market per year. Such a recovery process solves not only the gypsum disposal problem but also alleviates the pressures of rising costs of sulfuric acid.

A new process[87] developed in West Germany involves recrystallization under controlled conditions by the addition of certain compounds. The product can be dried and sold to a plaster of paris distributor or directly cast as plaster board or construction blocks. The final product from the synthetic gypsum compares favorably with most products made from natural gypsum. In addition, the requirements for labor, space and utilities are very much less.

In order to conserve the sulfur or sulfuric acid, nitric acid is used in the digestion of phosphate rock. Phosphoric acid (H_3PO_4), calcium nitrate $[Ca(NO_3)_2]$ and hydrofluoric acid (HF) are formed in this process[88] and the unwanted calcium nitrate is precipitated as gypsum by adding ammonium sulfate $[(NH_4)_2SO_4]$. The latter is regenerated and reused by treating the gypsum with carbon dioxide and ammonia and thus sulfate recycle is accomplished. Ammonia remains in solution as ammonium nitrate, a fertilizer ingredient.

Sulfur shortage has sparked renewed interest in nitric acid treatment of phosphate rock[89] to produce fertilizers. There are a number of processes available. Nonsulfur-consuming nitrophosphate generally involves larger investments but smaller operating costs than the sulfur-consuming processes.

Use of gypsum for sulfur production to fill the sulfur gas is being studied[90] by variations of standard ore-winning techniques or bacteriological digestion methods. These studies are directed to produce sulfuric acid or ammonium sulfate. In the wet process for phosphoric acid production, production of uniform gypsum crystals permits fast filtration, minimum sealing and modest requirements for site space, power and maintenance. Therefore, it was possible to cut down the capital and operating cost by 15%.

Nitrophosphate processes, which use nitric acid to dissolve phosphate rock, are becoming increasingly popular as a result of the current sulfur shortage. A Norwegian firm [91] has made major improvements in this field and is producing a wide range of fertilizers with high water solubility.

Dorr-Oliver has come out with a process that uses sulfuric acid acidulation of phosphate rock without appreciable consumption of sulfur. Instead of letting sulfur out as gypsum, the new process converts gypsum into calcium carbonate ($CaCO_3$) and reacts co-product ammonium sulfate $[(NH_4)_2SO_4]$ with fluorosilicic acid vapor derived from the phosphate rock to generate sulfuric acid for recycle to the rock acidulation step.

Animal Products

Meat-packing industry is a major one in this category and includes the following:

1. Slaughtering plant.

2. Meat-packing plant.

3. Meat-processing plant.

A slaughtering plant is a killing and dressing plant which does almost no processing of by-products. A meat-packing plant is both a slaughtering house and a meat-processing plant. Packing houses involve cooking, curing, manufacture of sausage, rendering of inedible fats into greases and many others. A meat-processing plant does no slaughtering at all.

The fundamental industry processes are shown in Figure 16. Blood is one of the major sources of BOD and, therefore, the recovery of blood is an important subprocess to the process of killing. Failure to recover blood increases the BOD by 72%. It is estimated that about 96% of the meat-packing industry is practicing blood recovery. Blood can be concentrated or dried and utilized in feeds

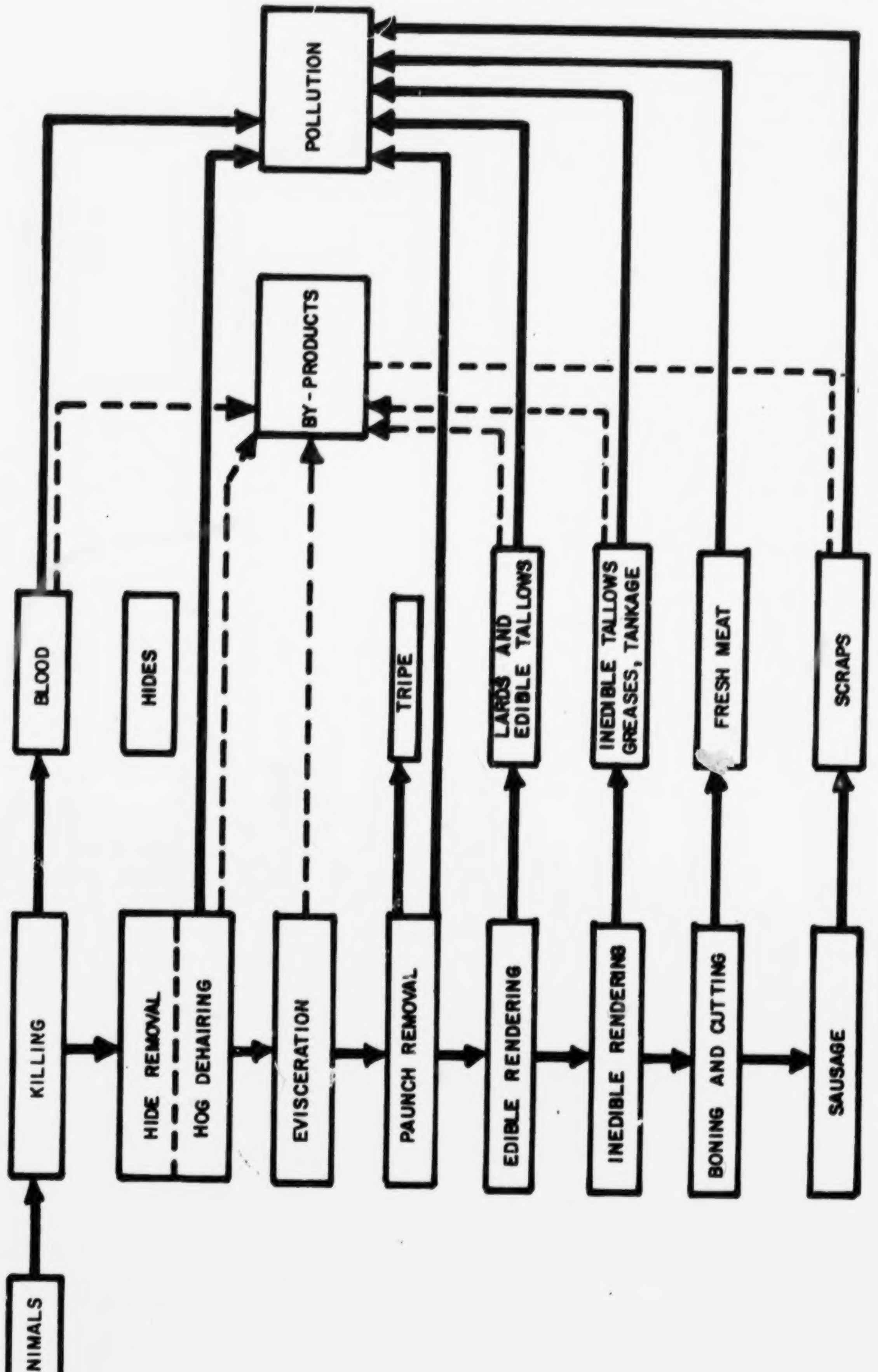
LIVE ANIMALS
KILLING
BLOOD
HIDE REMOVAL
HOG DEHAIRING
HIDES
EVISCERATION
PAUNCH REMOVAL
TRIPE
EDIBLE RENDERING
LARDS AND EDIBLE TALLOWS
INEDIBLE RENDERING
INEDIBLE TALLOWS GREASES, TANKAGE
BONING AND CUTTING
FRESH MEAT
SAUSAGE
SCRAPS
BY-PRODUCTS
POLLUTION

FIGURE 16

BASIC PROCESSES IN MEAT PACKING INDUSTRY and fertilizers[92].*

Hairs of hogs are removed by mechanical scrapers and they are sold, hauled to offsite disposal or dissolved in caustic solution. The trend seems to be toward sale because it can be used in the manufacture of foam rubber and felt. In summer, when the hair and bristles are short, they are disposed of at the incinerator as they are of little value.

Viscera are removed and distributed to the proper channels depending upon whether they will become an edible or inedible product.

Rendering process is of two types: edible and inedible rendering. In the edible rendering, fats are converted into lard and edible tallow. Edible rendering is applied primarily to hog fats, but also to some beef fat. In the inedible rendering scraps, trimmings, and inedible organs are converted into inedible fats which are used in soap, in the manufacture of grease and in animal feeds. Inedible rendering also provides an outlet for those parts of an animal which have been condemned by federal meat inspectors. Through rendering, condemned material is sterilized and converted into recoverable products. In recent years, the disposal of paunch manure is a vexing problem. Paunch manure contains very little fat and a large quantity of partially digested material. The paunch content of cattle is estimated at 40 to 60 pounds per head and contains about 1/3 pound of BOD[93]. In most cases, paunch solids are disposed of directly to farmers as fertilizer or as land fill.

Scraps generated in the manufacture of sausage are used in the rendering process. Grease and fats recovered in meat processing are valuable raw materials for soaps, gelatin and glue.

The wastes from industries producing fatty acids and glycerine contain a large amount of grease. Improper design of interceptors result in the discharge of a large fraction of grease. It was shown in many cases that by recovering the grease through the installation of proper interceptors that the yield can be increased by about 3% and the problems connected with sewer clogging, treatment process upset are solved satisfactorily.

In the wool pulling and wool scouring industry, valuable sheep skins and wool fibres have been recovered by the provision of proper screening arrangement.

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*If the protein values of the feed and fertilizer ingredients produced at the plant are higher than the requirements of the particular fertilizer being produced, some quantities of lower grade materials are sometimes blended with these materials.

The major concern in the poultry waste disposal is the high concentration of solids and fat. Centrifugal solid separators are used for the recovery of high solids and fat. An approximate materials balance of the system[94] indicates that at a waste input of 3200 gph, about 400 pounds per hour of solids are removed and 125 pounds per hour of fat recovered. The insolubles content of the influent was reduced from 10,000 mg/l, or higher, to 1500 mg/l. The fat content was reduced from 0.9% to 0.04%. The fat, thus recovered, is used in the dog food manufacturing process and solid matter disposed of at local rendering concerns. The returns from the by-products are above the operating costs and the recovery system proved economical.

In areas where there are no rendering firms, the by-products are removed from the gross pollution load of the plant and are given free in exchange for hauling them away.

In the leather tanning and finishing industry, very little water is reused. It appears that the practice of water reuse as a pollution reduction measure has been neglected in the average industry. The methods that could be used to reduce the quantity of process water are as follows:

1. Use of countercurrent washing techniques.

2. Clean-up and reuse of process waters.

3. Wash sprays instead of baths.

4. Automatic controls on process water.

5. Dry waste disposal instead of water carriage.

The following chart details normal by-product utilization in a tannery[95].

Item	Use
Trimmings, bellies and others	Used for edible purposes, oil production after rendering, protein feed after rendering and gelatin manufacture
Hair	Used in manufacturing, upholstering and rug backing
Fleshings	Glues
Degreasing exhaust Drum liquors	Reuse of solvent in tanning, soap
Spent lime liquors	After settling, the sludge can be mixed with other plant wastes and sold as fertilizer
Pickle solution wastes	In the past, this solution has been reused within the tannery for pickling a number of times. However, tendency of late has been to omit this reuse through advent of drum bate, pickling and chrome tanning
Chrome tan liquors	a) Holding and reusing in tannery b) Precipitate chromium hydroxide $[Cr(OH)_3]$, filter redissolve chromium with sulfuric acid. Considered economically impractical
Spent vegetable fans	Evaporated and sold as boiler compounds
Spent tan bark	Used as floor coverings for horse shows, circuses, playground. Sometimes used in paperboard manufacturing or in making white lead

Organic Chemicals Industry

In the organic chemicals industries, the wastes produced are high in COD and their treatability varies from treatable to most difficult to treat. These wastes contain valuable by-products and these are recovered[96].

New technology and process changes are, in general, directed towards better yield and, thereby, reduction in waste load. In cases where the by-product is valuable, product recovery is always practiced.

The organic chemicals industry is a complex one due to the number of products and processes utilized in the industry. All of these plants practice product recovery and waste reduction in one form or the other. To include all of them will be too elaborate and, therefore, the major ones are included here.

1. Acetaldehyde

   Acetaldehyde is produced by the Wacker process and waste discharge averages 1200 gallons per ton of product. The waste contains primarily chlorinated aldehydes and the COD is in the range of 10,000 mg/l. The waste is difficult to treat biologically unless it is diluted with other waters. Generally, several facilities handle these wastes by means of a deep well rather than by biological treatment.

   The waste discharge is reduced to 150 to 200 gallons/ton of product by suitable changes in the still design for final disposal either through deep well injection or incineration. In the concentration process, there is no reduction in the organic load and, therefore, the only possible means of reducing the organic load is recovery and use of the chlorinated aldehydes, dechlorination of the aldehydes or improvements in yield. The present trend seems to be in the emphasis on the improvements in yield and recovery and it is expected that the average yield will reach 97% in five years thereby reducing organic loading by about 40%.

2. Acetic Acid and Anhydride

   Light petroleum gas (LPG) oxidation results in the production of substantial amounts of other acids such as formic and propionic which must be disposed of by incineration, resale or biological oxidation. Unfortunately, resale of these materials does not appear to be practical because the markets for these chemicals are quite limited. Waste flow from this system is in the order of 1000 gallons/ton of product and the organic concentrations are in excess of 30,000 mg/l. In some operations, the stream is neutralized with caustic and the sodium salts of the acid are recovered.

Acetic acid and other higher acids are produced by oxidation of acetaldehyde. Water flows are of the same magnitude, but organic load is about 50% of the load generated by the oxidation of LPG. The Reppe process is another process for the production of propionic and other acids and the liquid waste amounts to about 50 gallons per ton of product including drains. The amounts and character of the waste would not appear to create serious waste treatment problems or expenditures. There will be improvements in the yield picture which will assist in reducing the waste management problems but it is not anticipated that any changes will radically change the waste situation.

3. Acetylene

The key factor in waste management in the production of acetylene from hydrocarbons centers around the control of the cracking furnaces to maximize the production of valuable products. The efficiencies are generally low--in the order of 40 to 50%--and efficiency improvements are therefore vital to the reduction of pollution load. Further, recoveries of waste products in burnable form is also vital to the effective operation of the unit. In some cases, a solvent is used to recover the acetylene. As solvent losses are usually significant, careful selection of the solvent and improved design of the vacuum stripper would assist in reducing the pollutional load.

4. Ammonia

The major streams arising from an ammonia plant are process condensate and site drains. The waste flow is 300 gallon/ton of product and ammonia lost in waste stream is 0.1 lb/ton of product. Removal of ammonia from waste streams is a necessity to eliminate eutrophication problems and recovery of ammonia has been proven practical. By air stripping of the waste after adjusting the pH with NaOH (about 0.1 lb/ton of product), it was possible to reduce the ammonia loss by about 60%. It is possible to remove greater amounts of NH_3 (90 to 95%) by increasing the air flow in the range of 500 to 1000 scf/gal., but such an approach is not economical.

5. Carbon Tetrachloride and Other Chlorinated Hydrocarbons

The major waste stream results from the production of hydrogen chloride as a by-product of the reaction. There is a great need for routes to the economic recovery of chlorine from hydrogen chloride or through the reuse of hydrogen chloride. A number of new oxychlorination processes have recently been developed which enable the user to utilize hydrogen chloride together with chlorine in a balanced facility. As an example, for the production of carbon tetrachloride (CCl_4):

$$CH_4 + 2Cl_2 \dashrightarrow CCl_4 + 2H_2$$

$$CH_4 + 4HCl + O_2 \dashrightarrow CCl_4 + 2H_2O$$

This approach eliminates the problem of hydrogen chloride (HCl), but does produce about 60 gallons of waste containing minor amounts of chlorinated methanes and HCl/ton of product. It is anticipated that, in the future, process changes will substantially eliminate the HCl being generated in these operations.

6. Cellulose Acetate

Major waste source arises from the stills used to recover acetic acid, acetone and other solvents. In addition, considerable amounts of degraded cellulose, phosphates (used as catalyst) and sulfuric acid (from spills) are generated. There are numerous opportunities for waste reduction in cellulose acetate production and the more important ones are the following:

a) Recovery and reuse of CA fines.

b) Improvements to achieve higher yields on cellulose.

c) Improved operation of acetone and acetic acid stills.

d) Use of additional stills to improve recovery.

7. Ethylene

In the production of ethylene, about 15 gallons of waste/ton of product are generated and this contains 2.5% sodium hydroxide (NaOH), 1% sodium sulfide (Na_2S) and 6.6% of phenols. Studies are underway to recover the alkali value from the spent caustic. There are no attempts at present for the recovery of sulfides but sulfide oxidation is generally practiced to reduce the immediate oxygen demand of this stream.

The process condensate stream may be reprocessed by being sent to a stripper and stripped by live steam. This will strip most of the non-phenol contaminants and about 20 to 25% of phenol. By contacting with fresh feed, it is possible to strip out most of the phenol which can be sent with the feed to the cracking furnace. The phenol-free waste water can be steam stripped to remove residual volatile hydrocarbons. The water stream, free of contaminants may be reused in steam generation in the plant.

The major products in the ethylene plants besides ethylene are propylene, low density polyethylene and alfa olefins. Spilled pellets and fluffs of polyethylene constitute a major pollution problem because of its unsightliness and reduction in the rate of oxygen transfer. A surface drainage separator with a basin and a baffle extending three feet below the water surface is used to trap the polyethylene. The trapped polyethylene is sent eventually to land fill for disposal.

Handling of quench water which constitutes 30% of the total plant effluent is difficult because it contains 1000 to 10,000 mg/l of oil in addition to finely divided coke and heavy tars. A part of the aromatic distillate co-produced in the plant as a solvent is used to extract the oil. The water is seperated from the solvent-oil mixture, filtered, degassed to remove hydrocarbon gases and sent to a surge tank. This water is used for cooling water make-up, which accounts for 10 to 15% of the cooling water for the plant.

8. Phenol

Major quantities of aqueous wastes containing organics and inorganics create considerable difficulties relative to waste treatment. A typical 100,000,000 lb/year phenol plant based on cumene produces a stream of 200,000 gpd of waste water containing 13,200 mg/l COD and 180 mg/l of phenol. Inorganics are produced at the following rates:

Sodium carbonate	-	5,000 lb/day
Sodium formate	-	500 lb/day
Sodium bicarbonate	-	500 lb/day
Sodium sulfate	-	22,000 lb/day

The waste production from the direct oxidation facility might be considerably less than the older process.

The following are practiced to reduce the waste load:

a) Careful control and modification of the process involved.

b) Recovery of inorganics by crystallization.

c) Recovery of phenol by solvent extraction.

As the sulfonation and chlorination approaches are reduced in importance, it is likely that the amount of waste generated per pound of phenol produced will be greatly reduced.

9. Urea

All of the major processes involve the high pressure reaction of CO_2 and ammonia. Typical wastes amount to about 120 gallons/ton of product with the following composition:

	lb/ton
Ammonia (NH_3)	3.6
Carbon dioxide (CO_2)	0.6
Urea (NH_2CONH_2)	0.8
Ammonium carbamate ($NH_4CO_2NH_2$)	0.1
Total	5.1

It is normal practice to remove about 50% of the ammonia by airstripping after adjusting pH with alkali. Recently, two new processes have been developed which strip the ammonia and carbamate by contacting with either NH_3 or CO_2 and sending the overload to the reactor. This approach reduces ammonia losses by 50% or more with a more drastic effect on carbonate.

10. Production of Chlorine from Hydrochloric Acid

In the conventional electrolysis process for producing Cl_2, 1.13 tons of NaOH are produced for every ton of chlorine produced. There is a greater demand for chlorine compared to NaOH and, therefore, there exists a chlorine-caustic imbalance. In order to avoid the imbalance, a new process called "KEL-CHLOR" has been developed by the Kellogg Company from the Deacon process and this process shows the possibility of making chlorine compounds. Hydrochloric acid produced as by-product in industries and not utilized may be used for the efficient and economic production of chlorine.

The following is a list of sources for HCl:

a) Production of HCl from inorganic sources.

b) Organic chlorination produces HCl as a by-product.

c) $MgCl_2$ can be hydrolyzed by hot steam to give MgO and HCl.

d) Ammonium chloride, a by-product of the Solvay process, can be dissociated to NH_3 and HCl and the two separated by a suitable method.

e) Hargreaves process, which uses SO_2 and air instead of H_2SO_4, could be used to produce HCl from NaCl.

f) When KCl is converted to potassium phosphate and nitrogen oxides in order to eliminate plasmolysis of the plants, HCl is produced as a by-product.

The process is shown in Figure 17 and, in this process, HCl is oxidized by pure oxygen in the presence of oxides of nitrogen which act as catalysts. H_2SO_4 is used as a catalyst carrier to absorb water. Employing this process, the pollution problems associated with small producers of by-product HCl can be alleviated. The chlorine from these small units would be small in amount and might not be competitive in the market place, but it could be used internally.

The economics of the Kel-Chlor process keep improving as the plant increases in size. Capital cost requirements go up approximately as the six-tenths power of the capacity. The by-product HCl from a series of different chlorination steps can be combined to provide feed for the Kel-Chlor plant. In summary, this new process can improve the economics of making chlorine compounds and has the possibility of making chlorine on a large scale by non-electrolytic methods. It can also alleviate the problem of caustic-chlorine imbalance and adjust caustic production to market requirements. It is also hoped that the economics of chlorination will be considerably improved and this should promote the use of chlorine compounds in the competition of markets such as replacing glass containers by copolymer of propylene and vinyl chlorine.

11. Anhydrous Hydrochloric Acid from Chlorinated Organic Waste

A variety of chlorinated organic residues are left behind as unwanted co-products after the manufacture of some big-volume chemical products. Examples: ethylene dichloride from vinyl chloride, benzene hexachloride from some insecticides, tetrachloro-ethylene from herbicides, and dichloropropylene from propylene glycol, chlorinated elastomers and nylon. The disposal of these wastes is a difficult problem and the methods already tried include: deep-well injection, ocean dumping, burning in open pits, lagooning, and burying. Disposal in deep wells is expensive and has hazards in some form or the other. Because of the toxic fumes emitted, open-pit burning of these wastes has been forbidden in several

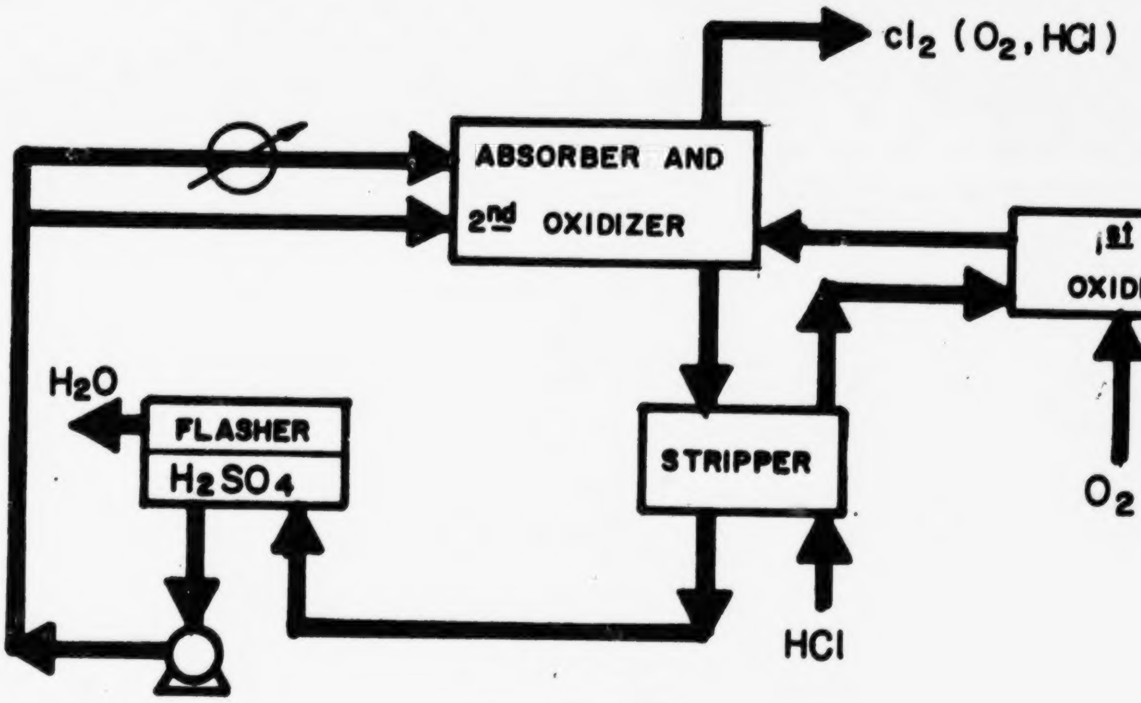
Cl_2 (O_2, HCl)
ABSORBER AND
2nd OXIDIZER
1st
OXIDIZER
H_2O
FLASHER
H_2SO_4
STRIPPER
O_2
HCl

FIGURE 17

FLOW DIAGRAM OF KEL-CHLOR PROCESS

states. Thus, there is a pressing problem of disposing of the one billion pounds of waste generated each year in the United States in the production of chlorinated organics.

Union Carbide's incineration - scrubbing system[97], shown in Figure 18, is recovering 99% of the HCl formed in the incinerator as 18° Be'. Alternatively, Carbide offers a unit with a stripping system to convert the product acid into anhydrous HCl. In either case, the venting gas stream will conform to most state regulations; and with additional scrubbing stations, its HCl content can be slashed from 1000 mg/l down to 50 mg/l. The operating costs are estimated at about 10¢/gal., in the upper limit of the 5 to 10¢/gal. range of conventional disposal costs. However, the system has the advantage of producing a saleable by-product in addition to meeting the anti-pollution requirements.

Table V summarizes by-product recovery in the organic chemicals industry.

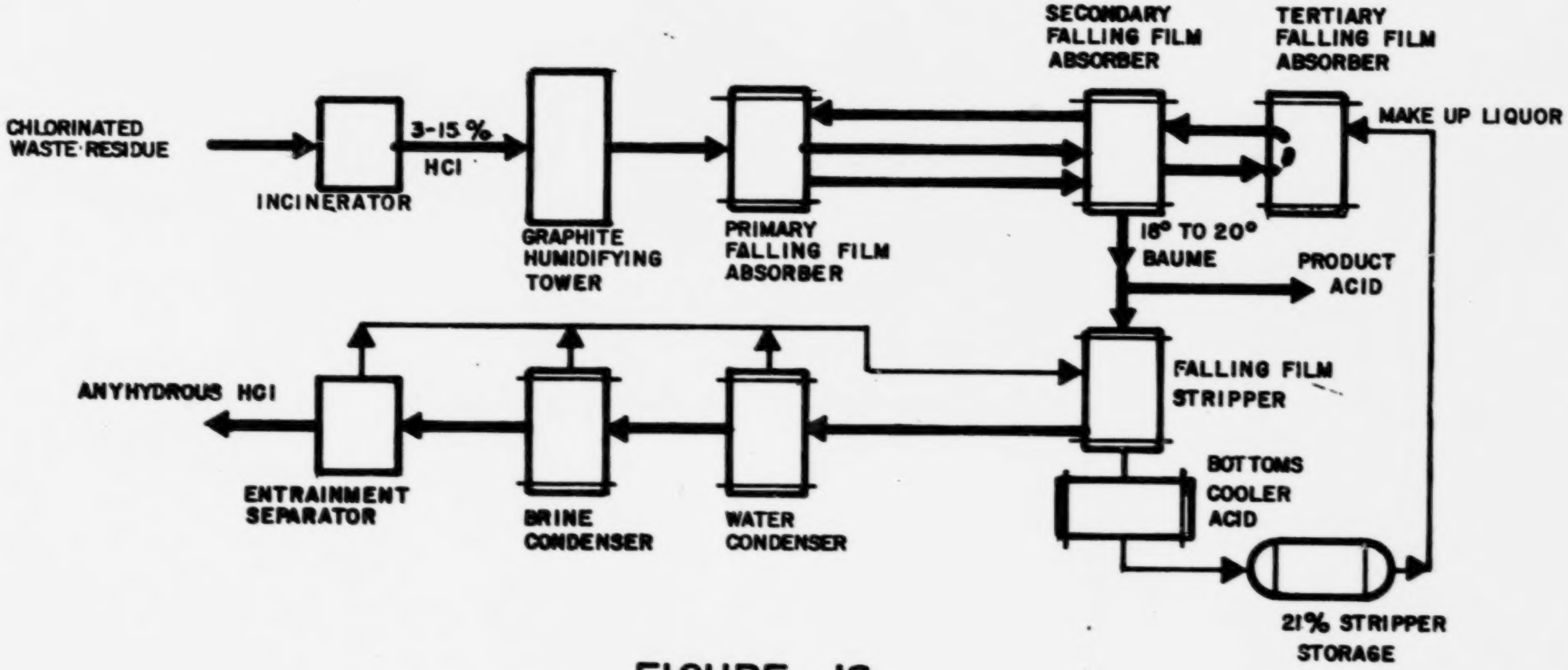
CHLORINATED WASTE RESIDUE
INCINERATOR
3-15 % HCl
GRAPHITE HUMIDIFYING TOWER
PRIMARY FALLING FILM ABSORBER
SECONDARY FALLING FILM ABSORBER
TERTIARY FALLING FILM ABSORBER
MAKE UP LIQUOR
18° TO 20° BAUME
PRODUCT ACID
FALLING FILM STRIPPER
BOTTOMS COOLER ACID
21% STRIPPER STORAGE
WATER CONDENSER
BRINE CONDENSER
ENTRAINMENT SEPARATOR
ANHYDROUS HCl

FIGURE 18

INCINERATION - SCRUBBING SYSTEM (UNION CARBIDE)

TABLE V

BY-PRODUCT RECOVERY IN THE ORGANIC CHEMICALS INDUSTRY

	By-Product Recovery			
Process	By-Product	Quantity	Value	Diminution of Pollutional Load
Acetaldehyde	Acetaldehyde	5 lbs/100 lbs	$0.50	40%
Acetic acid	Formic & Propionic acid	200 lb/ton	$20.00	60%
Acetylene	Solvent	10lb/ton	$5.00-10.00	10-30%
Ammonia	Ammonia	0.1 lb/ton	Negligible	60%
Carbon tetrachloride	Chlorine	0.4 lb/lb	1.2¢/lb	50-100%
Cellulose acetate	Cellulose fines	0.1 lb/lb	$0.01/lb	30-40%
Ethylene	Caustic	2 lb/ton	$0.04/ton	30-50%
Phenol	Sodium carbonate	2 lb/ton	$0.04/ton	15%
	Sodium formate	0.2 lb/ton	$0.04/ton	1%
	Sodium bicarbonate	0.2 lb/ton	$0.04/ton	1%
	Sodium sulfate	8 lb/ton	$0.16/ton	50-80%
Urea	Ammonia	3.6 lb/ton	$0.10/ton	50%
	Urea	0.8 lb/ton	$0.02/ton	20%
	Ammonium carbamate	0.1 lb/ton	$0.01/ton	10%
Chlorinated organics	Hydrochloric acid	Varies	Varies	80-100%

Textile Industry

The textile industry, as a whole, is a major factor in the American economy. The finishing operation of the textile industry produces a large amount of liquid wastes containing pollutants. Due to the tremendous growth rate in this industry, it is anticipated that more efficient manufacturing processes will be utilized, a larger percentage of the waste will be treated due to the increased pressure by regulatory agencies at all levels.

Process water reuse and recovery of by-products are the two major attempts being made in this industry in addition to process modifications to reduce pollution load and increase the economy.

The textile industry is grouped in three major categories for convenience:

1. Wool weaving and finishing.
2. Cotton textile finishing.
3. Synthetic textile finishing.

In the wool weaving and finishing industry, approximately 5% of its process water is reused. It is anticipated that countercurrent scouring can reduce the amount of water required by as much as 6000 gal./1000 lb of wool and use of rinse waters in the wash after fulling can reduce water requirement by 4000 gal./1000 lb of wool[98]. By-product recovery is limited because of the poor market for the products recovered. It is estimated that fifty to one hundred thousand tons of wool grease and 20,000 to 40,000 tons of suint could be recovered for production of lanolin and potash from wool and grease, respectively.

In the cotton textile industry, about 16% of the process water is reused. It appears that the process water reused will increase in the future because newer machinery is often of continuous or countercurrent design. Also, because process water is becoming more expensive in many areas, increased emphasis for reuse of process water is made. There is no significant by-product use of wastes in this industry. Many attempts have been made in the past to develop economically feasible methods for recovery of the expensive dyeing compounds but were unsuccessful. It is not hoped, in the foreseeable future, that any by-product be recovered for use on any significant scale.

About 10% of its process water is reused in the synthetic textile finishing industry. Even though there appears to be an adequate market for wastes reclaimed in this industry, there are no economically feasible methods available now. All liquid wastes contain chemicals used in the finishing itself and could be reused if reclaimed. All carriers are recovered and reused. Chemicals such as spent developed dye bath are not reclaimed as it is not economical. In the future, thermal wastes can be reused by heat transfer method.

Mercerizing of cotton yarn (treating with concentrated solutions of sodium hydroxide), results in a waste containing about 2% sodium hydroxide. This represents an important loss of this valuable chemical because of the relatively high chemical costs. Also, the alkalinity of the waste was very high requiring increased consumption of alum.

In a textile mill in Argentina[99], the waste stream containing sodium hydroxide was segregated and sodium hydroxide recovered by subjecting the waste to physical processes. Filtration of the waste prior to evaporation and two-stage evaporation were found to cause corrosion problems due to high temperatures. In the first stage of evaporation, the unit works at atmospheric pressure and, in the second stage at 25 in. Hg vacuum. The average concentration at the end of each stage is 5.2 and 25.0% by weight, respectively. The concentrated sodium hydroxide is filtered through a pressure filter and stored for reuse. The main goal of recovery of sodium hydroxide was the economics due to the high replacement cost of this chemical. Total amount of sodium hydroxide recovered amounted to 140 tons/year and the net profit obtained through recovery amounted to $22,000/year. An additional benefit resulting out of sodium hydroxide recovery is the decrease in consumption of alum at the treatment plant.

Nuclear Plants

The recovery of uranium and other fissionable materials from depleted nuclear-power fuels is necessary since only a fraction of the fissionable material is consumed prior to removal from the reactor.

The fuel is dissolved in nitric acid or any other acid before recovery. Sometimes fuels are mechanically decladded or oxidized prior to acid attack. The various products such as uranium, plutonium and other products, are separately recovered by solvent extraction employing an intricate set of pH adjustments. Efforts to recover fission products are now commercial. Most radioisotopes are not prepared in this manner but could be recovered from wastes by chemical action or ion exchange.

The Canadian nuclear power industry[100] uses heavy water reactors fueled with natural uranium. The spent fuel contained plutonium, a potential fuel, but the cost of recovering it was such that it was not competitive with natural uranium which is in abundance in Canada. The spent fuel is stored in zirconium cladding, under water at the reactor site for final disposal. If the price of uranium rises sufficiently, it will become profitable to recover the plutonium.

A fluoride volatility process has been developed[101,102] in which the fuel is treated with oxygen, hydrochloric acid or chlorine. This removes the cladding material as the volatile chloride. Fluorine is then added and uranium and plutonium leave as the hexafluorides which may be separated due to differences in their relative volatilities.

A new reclamation process[103] by Isochem, Inc., extracts and converts the plutonium content of metal scraps and sundry wastes from nuclear plants into a high purity plutonium nitrate solution. The scrap is initially dissolved in hydrofluoric acid, nitric acid and aluminum nitrate monohydrate. The dissolved plutonium is extracted with organic solvents and the plutonium-rich organic phase is stripped with nitric acid and concentrated to a final product having a plutonium of 200 to 300 gm/l.

Milk Industry

In the milk industry, approximately fifteen billion pounds of fluid whey results per year[104]. Because of its high COD and production of undesirable conditions, the whey has to be evaporated, processed and some returned to the farmer as slops.

Cheese whey has an average composition of about 4.8% lactose and 0.9% protein and, therefore, many useful by-products could be obtained. However, the demand for these by-products is not large enough to utilize the surplus whey. Conversion of whey to yeast to be used as a source of protein in animal nutrition is very attractive, but the cost of production is expensive. However, the economic factor becomes less important from the point of view of disposal of a potent waste.

Inorganic Chemical Industry

It is usually quite difficult to separate, in the inorganic chemicals industry, the practice of by-product recovery from normal production modes since so many of the industry's products are produced from ores or brines, the treatment of which produces a variety of materials other than the main product which is being sought. If the subsidiary material is also recovered, one might say that by-product recovery is being practiced. Speaking to someone familiar with the industry would indicate that this is not considered to be the case.

In addition, there are many inorganic chemicals which are routinely produced as by-products and where upwards of 90% of the total United States' production results from such activity. Among these are the following:

1. Sulfuric acid is reclaimed from petroleum alkylation units on a commercial basis and reclaimed by thermal means.

2. Ammonium sulfate is produced from coke oven wastes and other sources.

3. Calcium chloride and sodium chloride are frequently the by-product of fractional crystallization for other products and the neutralization of acid chloride wastes. OSW has said that Solvay process wastes can be crystallized to produce sodium and calcium chloride.

4. By-product hydrochloric acid arises primarily from the production of organic chemicals and this source represents 90% of United States production.

5. Sodium sulfate is the by-product of the production of hydrogen chloride by the Hargreaves process.

6. Fluoride salts are recovered from scrubber waters in the fertilizer industry.

Other situations also exist in this regard. For example, mercury is frequently recovered for reuse from the discharge of mercury cells for the production of caustic and chlorine by extraction. The recovery of ammonia in the production of soda ash by the Solvay process is vital to the economics of the process and this is performed by absorption. In the production of chemicals arising from brines such as sodium chloride, potassium chloride, potassium sulfate, borax, etc., a multitude of products are produced. Under some circumstances, a variety of products are produced and, in other circumstances, only a few of the potential products are utilized and the remaining brine is discharged to ponds. The recovery depends upon economics although certain materials such as the lithium salts are largely produced as by-products of other larger productive operations. The definition of by-product thus becomes clouded.

Ammonia could be produced as a profitable by-product from sea water desalting plants[105]. The study underway is looking at a theoretical three-way operation, namely, saline water conversion, power generation and ammonia synthesis. The project would be predicated on non-nuclear steam generators that would first produce power and fresh water. Left-over heat would then be used for ammonia synthesis. The recovery of chemicals from sea water, which is already practiced in the case of sodium chloride and iodine, is under consideration with regard to calcium and magnesium values--producing magnesium aluminum phosphate, for example.

The inorganic chemical industry's disposal problems center on the treatment of: sulfuric acid wastes, hydrochloric acid and hydrogen chloride wastes, and effluent gases containing acid oxides of sulfur, nitrogen and other elements.

Sulfuric acid wastes are common to many industries, and recovery is an accepted practice. When the impurity level is low, falling film evaporators are used and when the acid is dilute, it is utilized in or near the plant for the preparation of sulfates. When the solution is contaminated, dialysis, electrodialysis, adsorption, ion exchange, ion exclusion, ion retardation and crystallization are routes toward purifying and, in some cases, concentrating the acid. When contaminants are organic in nature, submerged combustion is used and SO_2 and SO_3 may be recovered from the effluent gas.

Inorganic acids used or produced in this industry create a serious waste disposal problem. Considerable efforts have been expended in some cases, such as in the production of vinyl chloride and chlorinated hydrocarbon, for the use of the acids in the process itself. Hydrogen chloride, in liquid or gaseous form, is produced as a by-product from the production of chlorinated organics and used in oxychlorination processes in place of chlorine. About 40% of waste hydrochloric acid, amounting to several million tons per year, is used in oil well activation, chemical and metal production, starch hydrolysis and cleaning applications.

By-product acid is produced by absorbing the gaseous hydrochloric acid in water in a graphite, tantalum or titanium absorber. Anhydrous hydrochloric acid is produced by stripping and condensation. Ion exchange is used for the regeneration of hydrochloric acid contaminated with metals[106].

In order to reduce the amount of waste hydrochloric acid, several processes have been modified or changed. One such process is the production of carbon tetrachloride (CCl_4) from carbon disulfide (CS_2) rather than from methane. Recovery of chlorine from hydrochloric acid has been practiced by electrolysis of hydrochloric acid, catalytic oxidation and a few others.

For the recovery of oxides of sulfur and nitrogen, wet scrubbing is commonly used as discussed in the section on the treatment of gaseous wastes. Other proposed processes to recover SO_2 or SO_3 are:

1. The Simon-Carves-Cominco process, based on wet scrubbing with ammoniacal solution to produce ammonium sulfate and either sulfur or sulfur dioxide.

2. The soda ash zinc oxide process, based on wet scrubbing with a soda ash solution that is regenerated with zinc nitrate ($Zn\ NO_3$) and lime - SO_2 is the product.

3. The manganese oxide process, based on wet scrubbing with a manganese oxide solution to produce SO_2.

4. Wet oxidation, based on the oxidation of SO_2 to SO_3 using ozone in a manganese sulfate solution.

5. The adsorption processes, based on the use of activated

charcoal in water, multi-bed charcoal adsorption, activated charcoal pipeline contactor and alkalized alumina.

The recovering of nitrogen oxides from the tail gases of nitric acid plants is accomplished by catalytic conversion to NO_2 and subsequent absorption. Other chemicals recovered include: boric acid by chelation from brine wastes, sodium sulfate from cracking-catalyst production wastes by crystallization, argon from hydrogen plants by fractional distillation, and silica from ferro silicon plants by air filtration.

Calcium chloride is obtained commercially as a by-product of chemical manufacture, principally the Solvay process, and from natural brines. The estimated annual production is in the order of one million tons. The overall equation for the production of soda ash by the Solvay process is:

$$CaCO_3 + 2NaCl \text{----------} Na_2CO_3 + CaCl_2$$

Most of the $CaCl_2$ is wasted into the streams except in some cases where it is evaporated and marketed for its calcium chloride content. The main applications of calcium chloride are in the laying of dust on highways and in low temperature refrigeration. The pollution due to calcium chloride is becoming less and less tolerated by the regulatory authorities and, therefore, recovery of calcium chloride would receive due importance in the future.

The potential for recovery in the industry is vast because the major water pollution problems of the industry relate to the presence of conservative species which must be removed in a concentrated form and disposed of by some means or other. As soon as tighter restrictions are established, recovery of these materials will be an obvious approach.

Table VI summarizes by-product recovery in the inorganic chemicals industry.

TABLE VI

BY-PRODUCT RECOVERY IN THE INORGANIC CHEMICALS INDUSTRY

	By-Product Recovery			
Process	By-Product	Quantity	Value	Diminution of Pollutional Load
Hargreaves	Sodium sulfate	0.6 ton/ton	$150/ton	50-70%
Caustic chlorine electrolysis	Mercury	Varies According to Cell		
Solvay	Ammonia	8-16 lbs/ton of soda ash		50-80%
Sea water desalting	Ammonia Sulfuric acid Hydrochloric acid	Varies Varies Varies		
Brines	Boric acid	Depends on brines		
Solvay	Calcium chloride	Depends on brines		
Magnesium salt production	Calcium chloride	Depends on brines		

APPENDIX I

GENERAL METHODS OF TREATMENT AND RECOVERY

Many techniques are available to treat wastes, and the application of a particular method or combination of methods requires an understanding, not only of each method and its limitations, but also of the composition and nature of the waste. Many methods discussed below are suitable for the recovery of waste products while others are final disposal techniques that preclude the recovery of wastes other than heat or water.

Methods of treating liquid wastes include:

1. Biological Reactions

   Biological reactions include biological oxidation and reduction and they occur as a natural part of the cell's metabolic cycle and involve enzymes. Bio-oxidation systems are commonly used in waste treatment facilities in the forms of trickling filters, activated sludge systems and oxidation ponds. Biological oxidations are inexpensive in operation and satisfactory for the removal of most organics. Sludge handling and disposal problems, difficulty of control, poisoning of the biology and inability to remove certain classes of organics are the major negative factors in this system. Oxidation ponds are not often aerated and depend on oxygen diffusion. When land costs are low, lagoons or oxidation ponds represent the cheapest satisfactory form of organic waste treatment.

   Biological reduction is accomplished by anaerobic bacteria and the reduction of organics results in the production of H_2S, CH_4 and CO_2. This principle is used in sludge digestion systems for the reduction of volume of sludge and production of sludge gas. Methane is the primary constituent of sludge gas and may be used to heat the digestion tanks, for space heating, for motor fuel, or may be used as a compressed gas.

   Biological reactions are important for chemical recovery as well as for waste disposal. Many industrial wastes such as paper and pulp mill wastes, brewery and distillery wastes, residues from the processing of corn and beet sugar are suitable as fermentation seeds. The products from the fermentation of these wastes are useful and include the following: drugs, vitamins, animal feeds, alcohols, acetone and flavor enhancers.

2. Chemical Reactions

Chemical oxidation has been used to treat wastes near room temperature but are limited in application due to high cost or low reactivity. The chemical oxidants and area of use are listed in Table A-I.

Incineration is a chemical oxidation process and has been applied to:

a. wastes containing organics in a number of contacting devices such as fluidized beds,

b. wet oxidation of organics at elevated temperatures and pressures,

c. thermal decomposition of inorganics in order to recover valuable components, as in the reburning of lime mud (arising in water treatment, sugar and pulp mill wastes) to recover lime,

d. thermal treatment of inorganics to recover valuable components, as in furnacing of kraft black liquor to recover pulping chemicals, and

e. oxidation of organics during the regeneration of adsorption and catalytic agents and of caustic solutions.

Table A-1 summarizes chemical oxidants and area of use.

TABLE A-I

CHEMICAL OXIDANTS AND AREA OF USE

S. No.	Chemical Oxidant	Area of Use
1	Air	Limited to easily oxidized pollutants such as sulfites and ferrous salts. Air may be used to agitate wastes and sweep out gases.
2	Ozone	May be used to oxidize most organics and many inorganics, but is limited by costs. Has been suggested for phenolic and cyanide wastes.
3	Chlorine, hypochlorite and chlorine dioxide	Used as a pretreatment or disinfectant. Chlorination has been used to treat cyanide, phenolic, textile, tannery, meat-packing and beet sugar wastes, and paper mill white water.
4	Electrolytic oxidation	Useful for oxidizing cyanides and for treatment of pickle liquors.
5	Permanganate and dichromate	Limited use due to high cost.
6	Hydrogen peroxide	Has been suggested for laundry, phenolic and cyanide waste.
7	Nitric acid	Suggested for treatment of ammonia-still liquors.

APPENDIX II

OTHER CHEMICAL REACTIONS OF INTEREST

Complexing

This has been suggested as a means of treating wastes and recovering by-products. The system has been applied to cyanide and pickling wastes and to the removal of iron and manganese from water supplies. The high cost of the complexing agent makes this process prohibitive.

Reduction

Chromates arising from plating baths are reduced with iron, zinc, brass or sulfur.

Precipitation

Heavy metals such as iron, copper, zinc and cadmium may be precipitated by the addition of alkalis. Chromium may be precipitated by the addition of a soluble barium salt, such as barium sulfide.

Neutralization

Many acidic wastes are normally neutralized with lime and other inexpensive alkali and alkaline wastes are neutralized by sulfuric acid and waste hydrochloric acid.

Solids Separation

Many industrial wastes contain solids and colloids, which may be removed for reuse or disposal by the application of gravitational forces or blocking functions. Gravitational systems depend on the tendency of particles to settle at rates dependent both upon their size and specific gravity differential between the particle and fluid. This principle is applied in equipment such as sedimentation tanks, thickeners, flocculation tanks, cyclones, centrifuges, screens, filters and sieving membranes.

Foaming and Flotation

Foam separation is analogous to solid - liquid adsorption, replacing the solid phase with a gas phase and including the important factor of entrainment.

In foaming, soluble surface-active agents gather at the solvent-air interface and the presence of air bubbles produces a foam which may be removed. If surface-active agents that complex heavy inorganic ions are added, these ions may be removed by foaming.

Foam separation technique has a great potential in sanitary engineering separation technology and can be used in the following:

1. Separation of ABS and organics from secondary effluents.
2. Removal of refractory materials from tertiary effluents.
3. Removal of radioactive metal ions.
4. Direct treatment of laundry wastes.
5. Removal of specific surfactants from industrial wastes, such as refinery and petrochemical wastes.
6. Separation of phenol from refinery wastes.
7. Recovery of heavy metals, such as Cr^{+6} in wastes from metal-finishing industries.

In flotation, air bubbles attach themselves to solids and carry them to the surface. This system removes both flocculated and unflocculated solids and the addition of a flotation agent results in better solid separation.

Adsorption

The contact between waste streams and high-surface-area commercial adsorbents will result in the removal of solubles from the waste as an adsorbed layer on the solids. Commercial adsorbents have large surface areas per unit weight, unsatisfied surface bonds to effect adsorption, and sufficiently large pores to permit diffusion of the adsorbate to most of the surface. They must also be either low priced or easily regenerated.

Adsorption may take place in columns, filters, agitated tanks or pipe lines. A few adsorbents that have found widespread acceptance include activated carbon and bone char, silica gel and activated silica, bauxite, alumina, clays and fuller's earth. Adsorption has been used in the treatment of organic-containing effluents from laundry, sewage, organic chemical and dye works, and in the removal of metal ions from plating baths.

Ion Exchange

Ion exchange is the reversible exchange of ions between a solid and liquid, in which there is no substantial change in the structure of the solid. These systems are usually operated by contacting the liquid with the ion-exchange resin in a column. The process is such that the pollutant ion may be recovered for use. Ion exchange has found application in the following as given below:

1. Recovery of chromic acid from cooling tower effluents.
2. Treatment of cyanide wastes--gives greater safety and costs less when compared to conventional methods of treating cyanides with chlorine.
3. Recovery and concentration of valuable metals such as silver, gold, platinum and nickel.
4. Recovery of metals from plating baths.
5. Treatment of low and medium level radioactive wastes.
6. Recovery of isotopes from high level radioactive wastes.
7. Recovery and removal of ionized organics from aqueous solutions.

Membrane Processes

Membrane processes are widely applicable to waste treatment. Three important and feasible processes are:

1. Dialysis: a separation method that utilizes diffusion as its driving force. In some cases, the membrence acts as a molecular filter. Dialysis has found application in the recovery of rayon from textile wastes, acids from spent liquor in the metal-treating wastes.
2. Electrodialysis: uses electromotive driving force. The ability of membranes to selectively pass either cations or anions is used in this process. Electrodialysis is used in the recovery of acid and iron from pickle liquor, and in the waste water recycle for the removal of dissolved solids.
3. Reverse Osmosis, or Ultrafiltration: uses a pressure gradient to make a separation based on the relative solubilities

and diffusivities in the membrane of the various liquid phase components. Reverse osmosis is used in the tertiary treatment and reclamation of waste water.

Solvent Extraction

Solvent extraction is not often used in waste treatment since it is expensive and not well suited to either treat large and varying volumes of liquid or remove trace quantities. Solvent loss is often responsible for high costs. However, solvent extraction is applied to ammonia-still wastes to recover phenol, wool wastes to recover wool grease, and pulping liquors to recover acetic and formic acids.

Evaporation and Crystallization

These processes involve separations by the formation of a new phase and are expensive when applied to dilute systems. However, evaporation is frequently involved in thermal oxidation processes in which organic-containing wastes are mechanically concentrated prior to evaporation, combustion and oxidation. Evaporation is useful in treating concentrated solutions but the application of evaporation to dilute solutions is limited to special cases such as the concentration of radioactive wastes.

Crystallization is involved in processes developed to treat pickle liquors and waste brines.

Ultimate Disposal

Ultimate disposal must be used for solid or highly concentrated liquid wastes that cannot be used or recovered. A large number of ultimate disposal methods are available and the choice depends on waste characteristics, economics and local regulations. A number of carefully developed studies have been made to determine the optimum means of disposing of wastes such as sewage effluent concentrate and sea water brine. Methods of ultimate disposal include the following:

1. Thermal oxidation - useful for organics and for stabilizing organic-inorganic mixtures.

2. Long-term biological oxidation and reduction - often not purposefully done but a natural consequence of other actions such as the use of sewage sludge for fertilizer.

3. Return to soil in a stabilized form - useful for most inorganic wastes.

4. Disposal into the ocean - common practice for plants and cities located near the ocean.

5. Deep-well injection - an extremely promising technique limited only by geology.

6. Encapsulation - limited to radioactive wastes.

7. Salt cavern storage - suitable for nuclear wastes.

8. Long-term tank storage - practical only for high level nuclear wastes.

9. Short-term lagooning - useful for reducing organic, nutrient and thermal loading but not a true ultimate disposal method.

APPENDIX III

PHYSICAL METHODS OF TREATING GASEOUS WASTES

Gaseous wastes generally find their way into liquid wastes through wet scrubbing or other processes. Various methods are practiced for removing solids from gas streams under a variety of conditions. The common devices used are based on a limited number of principles such as:

Gravitational force - Simple settler

Multi-gravitational force - Cyclone

Interference - Gas filters

Contact with a liquid phase (Scrubbing) - Venturi Scrubbers, etc.

Other external forces - Electrostatic precipitation, ultrasonics, etc.

Gaseous wastes are treated by taking advantage of molecular distributions such as:

1. Adsorption

   Gas purifications may be performed by adsorption and desorption cycles. Activated carbon, silica gel, alumina and molecular sieves find broad application.

2. Absorption

   The liquid scrubbing of gases is widely practiced for the recovery of SO_2 from power plants and sulfite mills.

3. Ion Exchange

   Some resins can remove pollutants such as SO_2 but are limited by temperature.

4. Membrane Permeation

   Several applications have been developed and employed in the separation or purification of gases. Use of thin silicone rubber membranes for the purification of gas streams, development of glass membrane and fluorocarbon membrane for the separation of helium from natural gas and production of hydrogen from wastes by permeation through a palladium membrane are some of the applications in the membrane permeation field.

5. Chemical Reaction

This is practiced to produce a more valuable, more collectable, or less harmful product. Removal of sulfur dioxide from power plant stack gases is a classic example. SO_2 is converted to SO_3 by chemical oxidation and, subsequently, removed. This conversion is necessary and beneficial because of the higher solubility of SO_3 and the value of sulfuric acid. The method is expensive and difficulties are often encountered due to low concentrations of the pollutant.

The most direct method for the removal of a reactive pollutant from a gas stream is to contact it with a reactive solid so as to fix the pollutant in a permanent or semi-permanent fashion. Use of lime, fly ash, or ferrous slag in a fixed, fluidized or pipeline reactor has been suggested for the removal of SO_2 but this appears to be expensive due to high pressure drops and poor solids utilization.

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